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SYNTHESIS OF CELLULOSE FILAMENT FOR RECYCLED FIBER REINFORCEMENT

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 25 July, 2016.

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Abstract of master's thesis

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Abstract

The objective of this master' thesis was to develop techniques for recycled fiber pre-treatments in order to produce both continuous cellulosic filaments as well as other nanocellulose structures. This exploratory work, therefore, investigated the properties of these materials in applications such as technical filaments and strength enhancers for use in papermaking, respectively.

Recycled fibers obtained from old cardboard was chemically pre-treated by either TEMPO oxidation or carboxymethylation and subsequently disintegrated into cellulose nanofibrils by using both homogenization and microfluidization. The surface hydroxyl groups (-OH) of the recycled, cellulosic fibers were successfully converted to carboxylic (-COOH) groups to different extent. The presence of carboxylic functional groups was confirmed by FTIR and conductometric titration. Homogenization and microfluidization were used in order to deconstruct the pretreated cellulosic fibers into small fibrils. The carboxymethylated fibers required higher mechanical energy than the TEMPO-oxidized ones. This was explained by the lower carboxylic group content introduced onto the fiber surface in the former system. The cellulose nanofibrils were examined via Scanning Electron Microscopy (SEM) and their size was assessed by the Atomic Force Microscopy (AFM). The nanofibrils were found to be 10-50 nm in width and several microns in length. From these efforts, it was concluded that nanofibrils can be obtained relatively easily from recycled fibers.

Two potential applications of the isolated cellulosic nanofibrils were addressed in this thesis. First, the production of continuous filaments by wet spinning and, secondly, the development of fibrils for deployment as additives for enhancing the mechanical strength of paper by addition in the wet-end. The filaments produced from cellulosic nanofibrils from recycled cardboard displayed slightly lower tensile strength compared to those from cellulose nanofibrils obtained from bleached virgin fibers. The addition of a co-adjuvant to the fibril hydrogel dope, namely, poly vinylalcohol, improved the dry and wet tensile strength properties of the filaments. More remarkably, however, was our finding in relation to paper strength enhancement: a significant improvement in mechanical strength (tensile strength, stiffness, and TEA) was observed upon addition of the nanofibrils to fibrt disperions followed by drainage and drying. In addition, lower paper surface porosity was measured. Provided the negative effects realized in dewatering are minimized, the results indicate a new potentially promising use for recycled fibers.

Keywords Cellulose filament, recycled fiber, TEMPO oxidation, carboxymethylation, microfluidization, wet-spinning, cellulose nanofibrils, strength, filament, strength additives

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List of Abbreviations

AGU	Anhydroglucose Unit
BD	Bone dried
CFS	Canadian Standard Freeness teater
CNF	Cellulose nanofibrils
DES	Deep Eutectic Solvent
DP	Degree of Polymerization
EDA	Ethylenediamines
FPR	First Part Retention
FPAR	First Part Ash Retention
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HCl	Hydrochloric acid
OH	Hydroxyl group
NaClO	Sodiumhypochlorite
NaBr	Sodium bromide
SDS	Sodium Dodecylsulfate
TEA	Tensile Energy Absorption
TEM	Transmission Electron Microscope
TO	TEMPO-oxidized
TOCNF	TEMPO-oxidized cellulose nanofibrils
WRV	Water Retention Value

Introduction

Paper recycling has attracted much attention in recent years due to environmental concerns and the need for sustainable development. Recycling processes generate approximately 55% of the pulp produced worldwide, since the process consumes less natural resources than the pulping process from wood (Delgado-Aguilar, Tarrés et al. 2015). Recycled fiber is generally retrieved from waste cardboard, newspaper, and office paper.

Recent applications of recycled fiber involve the use of cellulose nanofibrils (CNF) for forming continuous filament in textiles (Ma, Hummel et al. 2016) as well as strength additives in papermaking (Sehaqui, Ezekiel Mushi et al. 2012, Ma, Hummel et al. 2016). CNF have been produced using various pretreatment methods. 2,2,6,6-tetramethyl-1-piperidinyloxy radical-oxidized (TEMPO-oxidized) cellulose nanofibrils have been produced with homogeneous and uniform suspension (Isogai, Saito et al. 2011, Saito, Nishiyama et al. 2006). Recently, CNF have been isolated from pulp sludge by mechanical grinding, which consumes considerably more energy (Jonoobi, Mathew et al. 2012). Although much work has been dedicated to developing CNF from different materials (wood, bacterial, and tunicate), little research has been focused on recycled fibers. The use of pretreatment techniques promote disintegration of cellulose into fibrils.

The aim of the thesis is to develop a pretreatment technique for using recycled fiber in order to produce both continuous filament in several alternative materials as well as a strength additive for use in cardboard. CNFs are first isolated from recycled fiber by chemically modifying recycled fiber with TEMPO-oxidation and carboxymethylation techniques. Then, the pretreated recycled fiber is subsequently isolated with both homogenizer and microfluidizer in order to produce CNF. The nanofibrils are then used to form continuous filament by a wet-spinning method for potential use in textile applications as well as paper additives for papermaking.

The thesis is divided into four chapters. Chapter 2 reviews the literature about cellulose chemistry, pretreatment techniques for CNF and its applications. Chapter 3 describes methods used in the thesis. Chapter 4 presents and discusses the results. Finally,

Chapter 5 concludes by evaluating the potential for the materials developed in this thesis and suggesting directions for future research.

Chapter 2. Literature Part

This chapter describes the fundamentals of cellulose chemistry and also reviews the pretreatments techniques used in order to obtain the CNF as well as their applications. Section 2.1 and 2.2 describes chemistry and structure of cellulose and CNF, respectively. Section 2.3 explains recycling of paper and recycled fiber. Section 2.4 introduces pretreatments techniques used for producing CNF. Finally, Section 2.5 discusses the potential applications of CNF.

2.1 Theory of Cellulosic Fiber

Cellulose is one of the most abundant natural resources in the world. Cellulose is constituted by linear polymer chain composed of two repeating anhydroglucose units (AGU) which are covalently bound by β-(1,4)-glycosidic linkages (Klemm, Heublein et al. 2005). Cellulose can be found in most plants on earth but it normally extracted from woods. The hierarchical structure of wood is illustrated in Figure 1. The fundamental of cellulose ranges from the polymeric chain of glucose molecules, crystalline cellulose microfibrils, bundles of microfibrils, cell wall, fibers, tissue, and trees respectively (Fengel , 2011).

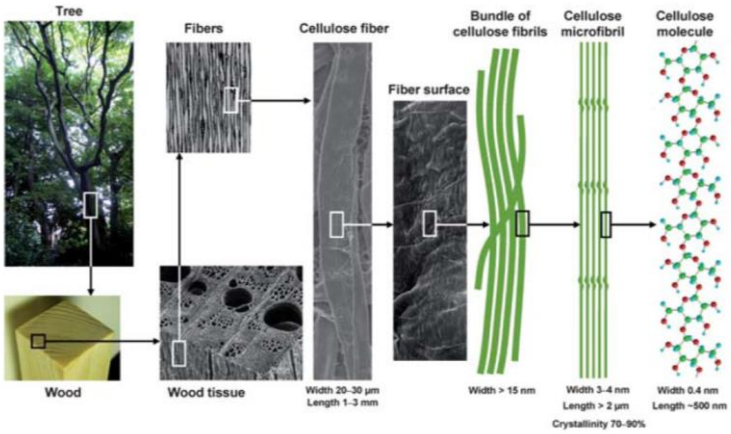


Figure 1 Hierarchical structural order of wood (Isogai, Saito et al. 2011)

The molecular structure of cellulose (as shown in Figure 2) is a linear-chain carbohydrate polymer with an extensive number of hydroxyl groups (three OH-groups

per AGU unit) and every second AGU is twisted 180° in the plane. The length of cellulose chain represents the number of constituted AGUs (Degree Polymerization, DP). In wood pulps, the degree of polymerization is normally ranged from 300-1700 and depends on the plant source (Klemm, Heublein et al. 2005).

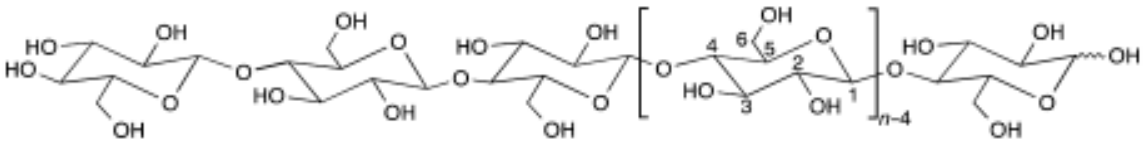


Figure 2 Molecular structure of cellulose (Klemm, Heublein et al. 2005)

From the molecular structure of cellulose chain, there are many functional hydroxyl groups (OH-groups) in cellulose chain. The OH-groups are located at both ends of the chain. These two groups also chemically react in different ways. At the C1, the OH-group is a reducing aldehyde hydrate as a result from ring formation of intramolecular hemiacetal bonding. The C4 position, the OH-group is non-reducing alcoholic hydroxyl group (Klemm, Heublein et al. 2005).

2.2 Cellulose nanofibrils

Cellulose nanofibrils (CNF) can be produced from cellulosic materials either from virgin fiber or recycled fiber. It has been produce through a fibrillation of fiber by mechanical force. The dimension nanofibrils, as shown in Figure 3, have diameter less than 100 nm, several micrometers in length, and also high aspect ratio. Generally, intensive mechanical disintegrations are required in order to individualize wood cellulose. High energy demand is inevitable for nanofibrillation due to numbers of inter-fibrillar hydrogen bonds. The fibrils have 3-4 nm in width after complete individualization or 20-100 nm after less profound homogenization (Isogai, Saito et al. 2011). Additionally, it is impossible to disintegrate cellulose into individual fibrils completely because numbers of hydrogen bonds are still present (Isogai, Saito et al. 2011, Saito, Kimura et al. 2007).

The structure of fibrils (shown in Figure 3) illustrate extraordinary mechanical properties with Young's modulus up to 198 GPa (Abe, Iwamoto et al. 2007) in crystalline structure and also exhibit low coefficient thermal expansion up to 10^{-7} K^{-1} in longitudinal directional (Abe, Iwamoto et al. 2007). Thus, the potential applications

of CNF are mainly related with reinforcement in composite materials or strength additives.

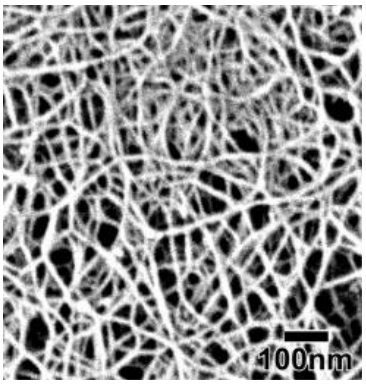


Figure 3 SEM picture of freezed-dried CNF (Abe, Iwamoto et al. 2007).

2.3 Paper recycling and recycled fiber

Paper recycling is the process of recovering cellulosic fiber by mixing waste paper with water and chemicals in order to disintegrate paper into recycled fiber. The process involves many unit operations as follows:

1. **Deflaking, repulping, and slushing:** to break down, disintegrate the recovered paper into a pumpable slurry
2. **Fractionation or screening:** to separate and remove unwanted contaminants (plastic, glue, and metal) from pulp slurry by particle size, and shape.
3. **Dispersing and kneading:** to reduce the size of specks, stickies, and ink into smaller size.
4. **Refining:** to modify the fiber structure in order to improve fiber properties by enhancing the interfiber bonding.
5. **Dewatering, thickening, pressing:** to remove water from pulp slurry for further specific process, such as, bleaching unit and storage.
6. **Bleaching, upgrading:** to enhance the physical appearance of recycled fiber by increasing brightness.
7. **Storage:** to prevent pulp suspension from settling down at the bottom of the storage tank.

After these processes, the recycled fiber then can be made into new recycled paper.

Recycled fiber starts its life from virgin fiber and is used repeatedly before it is eventually disposed as illustrated in Figure 4. Recycled fiber usually derives from two main sources: post-consumer waste and pre-consumer waste. The pre-consumer wastes are collected from over-issued, and converting wastes in the manufacturing process, such as shaving, cutting, and broke. In contrary, sources of post-consumer waste vary among different consumer waste streams, such as corrugated container, office paper, old newspaper, and liquid packaging. The recycling of paper has becoming more important because paper recycling saves clearly benefit rather than virgin fiber by saving energy and natural resources compared to production of virgin fiber.

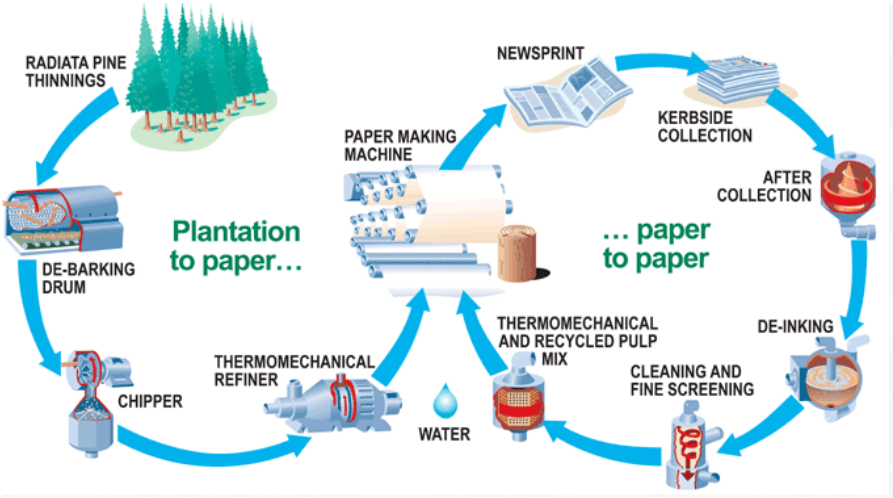


Figure 4 Origin of virgin and recycled fiber as well as their life cycle (Bowen Island Recycling Depot, 2007)

The recycling processes are usually more complex than the systems of virgin fibers for two principal reasons. Firstly, the reason is the recovered paper is a mixture of fibers from many sources (newspaper, old cardboard, office paper, liquid packaging). Secondly, waste papers contain various types of contaminants so the processes are designed to effectively remove those contaminants. It is possible to classify the contaminants from their origin as follows:

- Additives from paper production, for example, fillers, coatings, and process chemicals.
- Materials form applications, such as, foil, plastic laminations, printing inks, and adhesives.
- Mixed substances during paper's life cycle including stone, paper clips, and wire.

Separation processes need to be related to the types, particle size, density, shape, surface properties and characteristics. As a consequence, different unit operations are used for a specific type of contaminants. For example, the cleaner in recycling process is suitable to remove larger particles from pulp slurry by taking advantages of density of heavy particles as shown in Figure 5 (Göttsching, 1999).

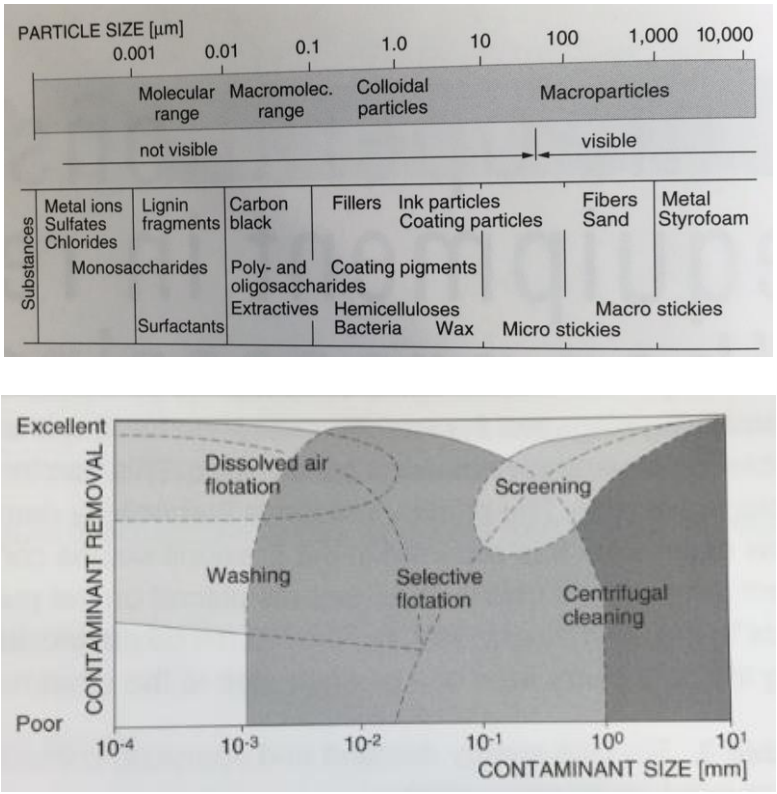


Figure 5 Size distribution and efficiency ranges of contaminants removal in paper recycling process (Göttsching, 1999).

2.4 Pre-treatment Methods

CNF are obtained from primary fibril isolated from the hierarchical structure of wood cell walls (Wang, Sabo et al. 2015). CNF in wood are normally attached as bundles with strong hydrogen bonding. This bonding makes it difficult to liberate individual CNF without pretreatments that enhance fiber swelling. After modification, the structure of cellulose are loosen and the adhesion force are reduced, which makes defibrillation of fibers into CNF easier and less energy-intensive (Saito, Kimura et al. 2007, Isogai, Saito et al. 2011). The generally utilized pretreatments comprise TEMPO-mediated oxidation (Saito, Kimura et al. 2007, Isogai, Saito et al. 2011), carboxymethylation (Eyholzer, Bordeanu et al. 2010), and enzymatic hydrolysis with endoglucanases (Wang, Sabo et al. 2015, Martin-Sampedro, Filpponen et al. 2012). In addition, novel techniques have been developed to overcome the hydrogen bonding in lignocellulosic materials. Micro-emulsion has been recently introduced by formulating the thermodynamically stable emulsions for destroying the hydrogen and covalent bonds and overcome the capillary forces in wood materials. As a consequence, the further isolation by mechanical treatments require less energy (Carrillo, Saloni et al. 2012, Carrillo, Saloni et al. 2013, Carrillo, Laine et al. 2014). Furthermore, the Deep Eutectic Solvent (DES) has been used to improve the swelling of cellulosic materials to improve mechanical disintegration as well (Sirviö, Visanko et al. 2015).

2.4.1 TEMPO-mediated Oxidation

2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) is the mediated oxidative chemicals and water-soluble used for oxidation of primary hydroxyl groups into carboxylic groups under mild conditions. The oxidative reaction could be completely modified into water-soluble polyglucuronic acid (Saito, Nishiyama et al. 2006). The hypothesis of oxidative reaction from hydroxyl groups to carboxylic groups via aldehydes proceeds from the mechanism shown in Figure 6. Numbers of oxidative reactions have occurred through mediated oxidation of primary hydroxyls to carboxylate groups (Isogai, Saito et al. 2011).

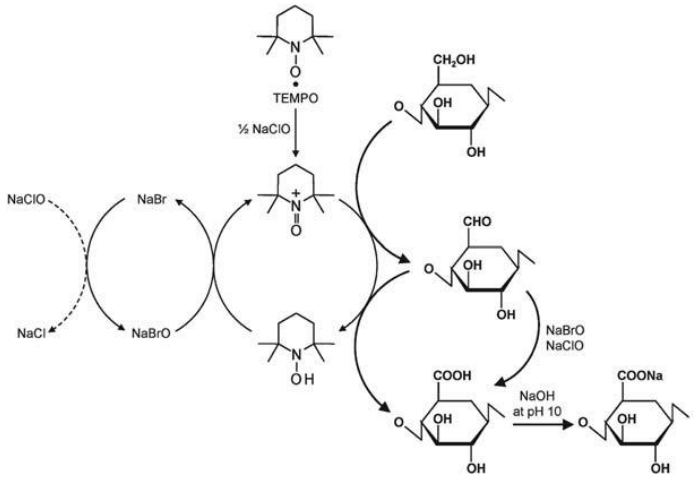


Figure 6 Oxidation reaction of primary hydroxyls to carboxyl groups with TEMPO-mediated oxidation (Isogai, Saito et al. 2011)

The significant amount of carboxylic and aldehyde groups introduced to celluloses are detected after TEMPO-mediated oxidation while the morphologies and crystallinities are remain unaltered. The additional carboxylic groups affects the negative charges of cellulose. As a result, the repulsive forces from carboxylated cellulose enhance the separation of CNF.

Saito (2007) and Isogai (2011) have modified the native cellulose to TEMPO-oxidized cellulose by using bleached softwood and hardwood kraft pulp (once-dried and never-dried pulp). The never-dried pulp is introduced to the solution of TEMPO, Sodium bromide (NaBr) and Sodiumhypochlorite (NaClO), then adjust the pH of solution to pH 10 by hydrochloric acid (HCl). After that, the pH is maintained by adding of Sodium hydroxide (OH) until its consumption ceases. The treated pulps are washed with deionized water and kept at 4^{o}C for further characterization. The suspension of treated pulps are diluted at 0.1% w/v for six to ten days for disintegration by magnetic stirring at 1500 rpm. The resulting solutions display that after ten days of dispersing the TEMPO-oxidized pulp is homogeneously dispersed as from the transparency of solution in Figure 7 (Saito, Kimura et al. 2007, Isogai, Saito et al. 2011).

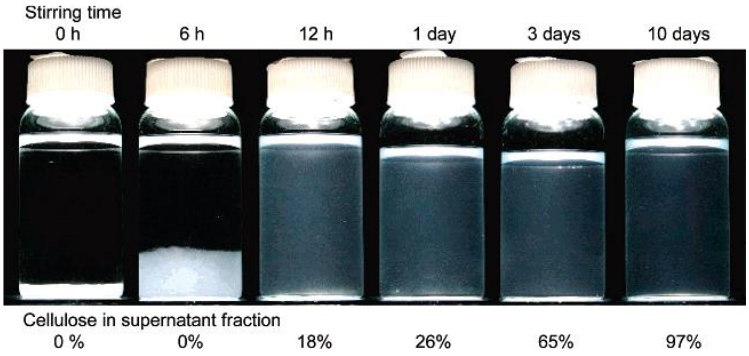


Figure 7 TEMPO-oxidized cellulose after stirring from zero hour to ten days (Saito, Kimura et al. 2007).

The effect of different carboxylate contents in never-dried and once-dried pulp also are also determined on the dispersion of nanofiber. At the carboxylated content up to 1.5 mmol/g, the transparent dispersion could be visually observed and such solutions are possibly maintained for longer than six months at about 4°C in a refrigerator (as shown in Figure 8). Consequently, the carboxylate content is the key factor affecting the dispersion of oxidized cellulose (Saito, Kimura et al. 2007).

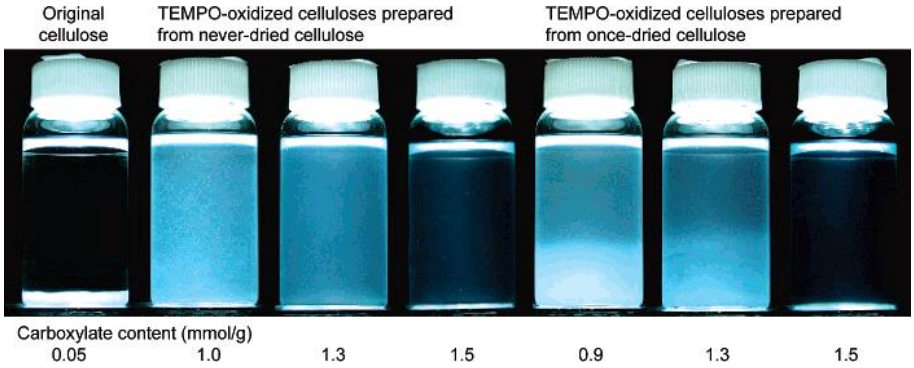


Figure 8 TEMPO-oxidized celluloses at different carboxylated contents (Saito, Kimura et al. 2007).

Characterization of CNF morphology with TEM shows that TEMPO-oxidized CNF comprise isolated single fibrils with diameters around 3-4 nm and widths of a few microns as illustrated in Figure 9. According to the small size of the cellulose, the highly viscous and transparent solutions could be obtained from the TEMPO-oxidation

method (Isogai, Saito et al. 2011, Saito, Kimura et al. 2007, Ishii, Saito et al. 2011, Saito, Okita et al. 2006).

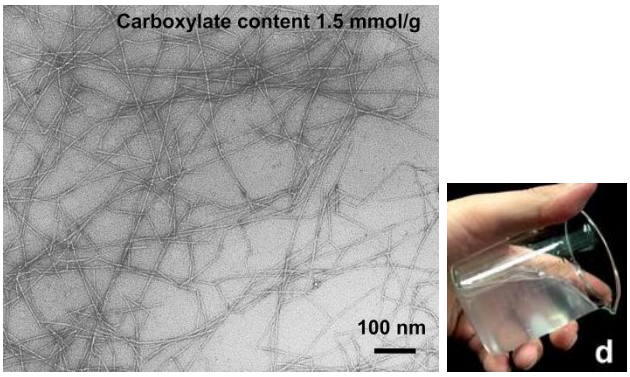


Figure 9 TEM image and picture of carboxylated cellulose at 1.5 mmol/g (Isogai, Saito et al. 2011, Saito, Kimura et al. 2007)

Isogai (2011) and Saito (2007) also compared the amount of carboxylate contents in oxidized never-dried and once-dried cellulose that there were no major different carboxylate content and oxidization time between them. Moreover, the Water Retention Value (WRV) of never-dried pulp displayed higher than once-dried cellulose for the carboxylate content between 0.05-1.3 mmol/g. The once-dried pulp illustrated reduced water-accessibility, less swelling, more collapsed fiber and decreased specific area. However, when the carboxylate content reached to 0.15 mmol/g, the WRV was quite similar for both never-dried and once-dried pulp. This caused from the oxidation of hydroxyl groups happened at the surface of fibrils only. The regioselective reaction possible yielded specific water-absorption behavior without alteration of cellulosic morphology (Saito, Kimura et al. 2007).

2.4.2 Carboxymethylation

Carboxymethylation technique also introduces carboxylic groups to the surface of cellulose. The negative charges from the carboxylic groups enhance the stable suspension of carboxymethylated pulp and promote the isolation of cellulose. Naderi et al. 2015 have studied the carboxymethyl modified cellulose in order to produce fibrillated cellulose. The study has shown that the carboxymethylated-modified pulp can be fibrillated at the same solids content where the fibrillation is usually done as

commercial CNF. The carboxymethylation reaction illustrated in Figure 10 has introduced the carboxymethyl (-CH_3COOH) groups to cellulose with chloroacetic acid (Eyholzer, Bordeanu et al. 2010, Naderi, Lindström et al. 2015).

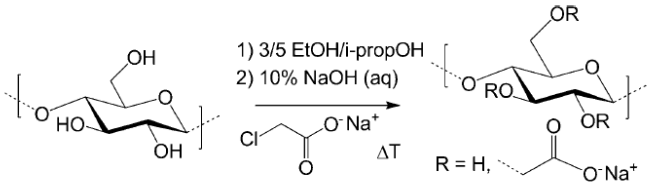


Figure 10 Carboxymethylation of cellulose with chloroacetic acid (Eyholzer, Bordeanu et al. 2010)

The FTIR spectrum has confirmed that the carboxymethylation introduces the negatively-charged carboxymethyl groups with the peak at 1595 cm^{-1} for C=O stretching and 3600-2800 cm^{-1} for –CH stretching (Eyholzer, Bordeanu et al. 2010). In addition, SEM images has shown less agglomeration of fibers after the modification as well (Figure 11). After pretreatment with carboxymethylation method, the orphological structure of fiber has not changed confirmed by SEM images (Khalil, Davoudpour et al. 2014). However, the multiple homogenizations may lead to minute aggregation of CNF. The elasticity, tensile, and modulus of CNF films are enhanced after two or three passes of homogenization. The film also exhibit the potential application in oxygen barrier film used in packaging (Khalil, Davoudpour et al. 2014, Junka, Filpponen et al. 2014).

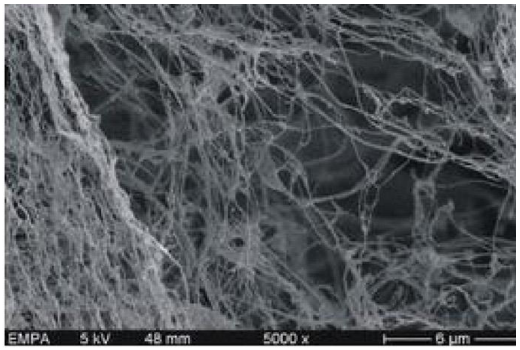


Figure 11 SEM image of redispersed of carboxymethylated fiber (Khalil, Davoudpour et al. 2014)

2.4.3 Enzymatic Hydrolysis

Pre-treatment with enzyme is another technique used for nanofibrils production. Normally, Endoglucanases are selected as enzymatic hydrolysis to specifically hydrolyze the interfiber-bonding in lignocellulosic materials. The use of enzymatic method could be lower the costs and environmental impact of CNF preparation by reducing both the chemical consumption and the number of energy-intensive passes through the homogenizer. Henriksson et al., 2007) and Pääkkö et al., 2007 have prepared microfibrillated cellulose from bleached softwood sulphite pulps via enzymatic pre-treatment and subsequently mechanical treatment. The virgin pulps are diluted to 3% consistency with Endoglucanase and 50 mM of tris (hydroxymethyl) aminomethane/HCl buffer to maintain pH at 7. The pulps are incubated at 50^{o}C for two hours, then stop the reaction at 80^{o}C for thirty minutes, and wash with deionized water as a final step. After that, the pulp are passed through the homogenizer to produce the microfibrillated cellulose. The characterization shows that Endoglucanase treatment followed by mechanical shearing can possibly produce microfibrillated cellulose with high aspect ratio as confirmed by AFM picture shown in Figure 12 (Pääkkö, Ankerfors et al. 2007, Henriksson, Henriksson et al. 2007).

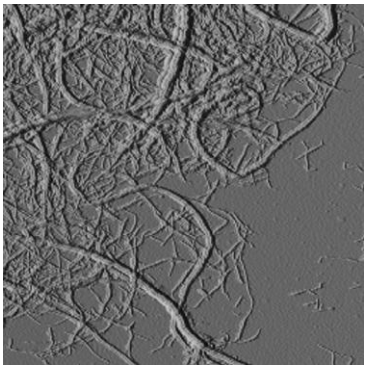


Figure 12 AFM image of enzyme treated pulp (Henriksson, Henriksson et al. 2007)

Pre-treatment enhances swelling of cellulosic pulp fibers in water suspension enabling the production of microfibrillated cellulose in a more environmentally friendly way. (Henriksson, Henriksson et al. 2007). Wang et al. 2015 also use endoglucanases to

pretreat virgin fiber to produce nanofibrillated cellulose in order to cast the film (Wang, Mozuch et al. 2015). From the TEM image, endoglucanase-treated fiber shows that the enzyme efficiently disintegrates the filament and the fibrillated cellulose has more uniform diameter in the nanosize (as shown in Figure 13). The resulting film prepared from the enzyme treated also displays more transparent with good thermal stability. (Wang, Sabo et al. 2015, Wang, Mozuch et al. 2015).

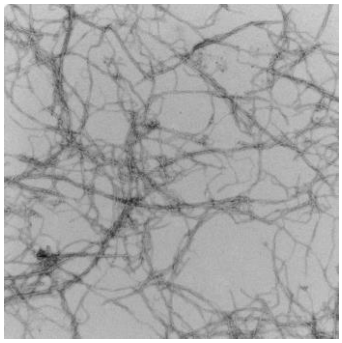


Figure 13 TEM image of endoglucanase-treated pulp (Wang, Sabo et al. 2015)

2.4.4 Deep Eutectic Solvent

Deep eutectic solvent (DES) is a new class of chemicals which can possibly perform as solvents, reactants, and catalyst simultaneously. The mechanism of DES can swell the cellulosic materials without altering their ultrastructure. DES is prepared by combination between halide salt of quaternary ammonium or phosphonium cation (considered as the hydrogen bond acceptor, HBA) and urea, glycerol, ethylene glycol (hydrogen bond donor, HBD). The distinct property of DESs is a lower melting point compared to the original HBA and HBD as the strong hydrogen bonding inhibits the parent compounds from crystallizing. Moreover, the toxicity of DES is considered as relatively low because the individual components has low CO_2-emission, and biodegradable. As a consequence, these characteristics of DES shapes them as potential solvent, and chemicals for sustainability (Sirviö, Visanko et al. 2015).

Sirviö et al., 2015) reported that DES could be used as a pretreatment method to separate CNF from bleached birch pulp. A mixture of choline chloride and urea was selected as the DES. This DES was heated to 100^{o}C to obtain a clear mixture. Then, oven-dried cellulose is added to the solution for a couple of hours for swelling and is

washed with deionized water. Finally, the treated pulps are passed through a microfluidizer. The result of DES-treated pulp slurry in water displays a swollen and gel-like material. However, the dried form of DES-treated pulp is visibly similar to the original bleached birch pulp as shown in Figure 14. After the disintegration by microfluidizer, it starts to form a turbid, homogeneous, gel-like fluid.

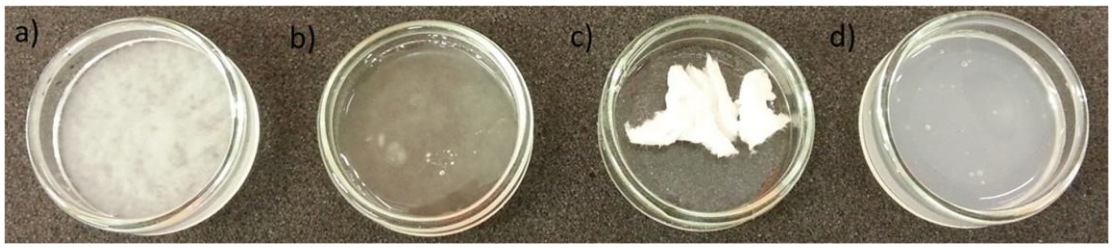


Figure 14 Cellulose suspension 1% in (a) water and (b) DES (c) DES treated pulp after washing and, (d) after mechanical disintegration (Sirviö, Visanko et al. 2015).

The cellulose structure and crystallinity after treatment with DES is still remain and no rearrangement of cellulosic structure into another crystallinity. Thus, this is also the affirmation that DES literally swells the cellulose while maintain the cellulose structure. Moreover, the spectra of DES-treated cellulose also illustrates as conventional native cellulose as shown in Figure 15 (Sirviö, Visanko et al. 2015).

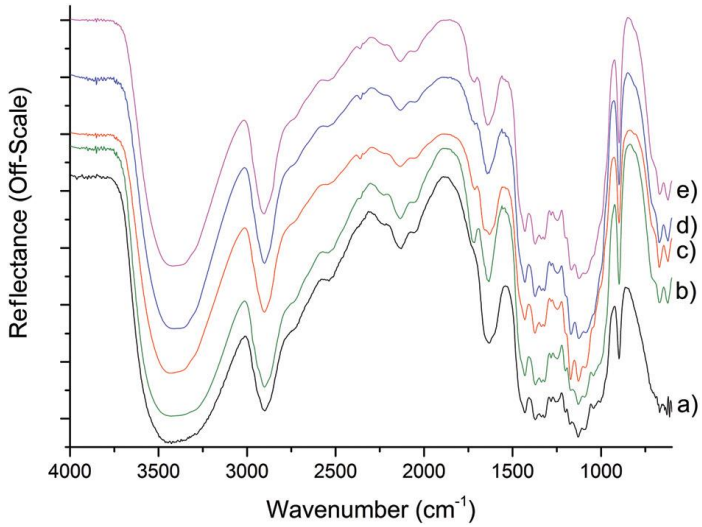


Figure 15 Spectra of a) native cellulose b) DES-treated after washing c) to e) after mechanical treatment (Sirviö, Visanko et al. 2015)

Tenhunen (2015) also uses DES for producing textile filament by swelling the native cellulose in DES. They also study the structure of cellulose after treatment with DES compared to the original. The result from the ^{13}C MAS NMR Spectrum indicates that the crystalline structure and chemical composition of cellulose and DES-treated cellulose are almost similar as shown in Figure 16. Moreover, there is no additional peak observed in the spectrum that illustrates no degradation of the cellulose (Tenhunen, Hakalahti et al. 2016). DES is also environmentally friendly and recyclable after washing from the pulp by simple evaporation (Abbott, Boothby et al. 2004).

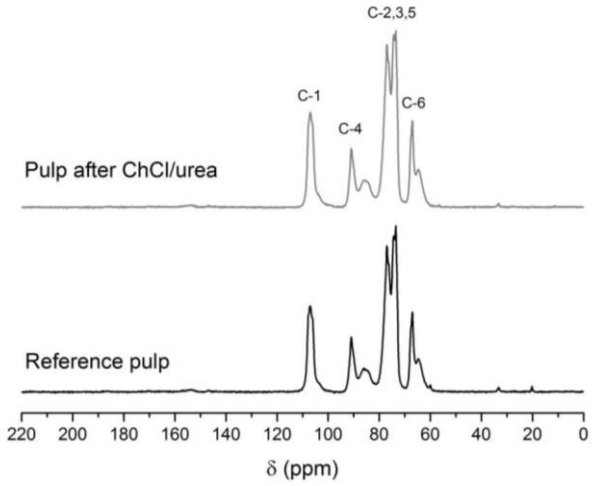


Figure 16 ^{13}C MAS NMR Spectra of bleached softwood pulp before and after treatment by Choline Chloride/ Urea (Abbott, Boothby et al. 2004).

2.4.5 Micro-emulsion

Micro-emulsion is one of the pre-treatment techniques used to weaken fiber structure for subsequent fibrillation process. The micro-emulsion systems are considered capable of penetrating the complex capillary structure of lignocellulosic materials. The micro-emulsions are the thermodynamically stable dispersions of two immiscible liquids which automatically form in the presence of a surfactant that reduces the interfacial force between the two phases. As a result, the micro-emulsion can overcome the chemical, and physical heterogeneity in lignocellulosic materials and

actually reduce the energy required in the mechanical disintegration (Carrillo, Saloni et al. 2013). However, the mechanism and effect on the penetration remains undiscovered (Carrillo, Saloni et al. 2013).

Carrillo et al., 2013 examine the micro-emulsion system used for pretreating of cellulosic materials. They discover that the media can effectively overcome the chemical and physical bonding in biomass. The thermodynamically stable emulsion are formulated to destroy the hydrogen bonding and reduce the energy required in the subsequent mechanical treatment. The surfactant (S) - oil (O) – water (W) are selected to formulate the micro-emulsions. Two active ingredients used for deconstruction of hydrogen bonding are urea and ethylenediamines (EDA). The compositions of micro-emulsions are shown in Figure 17 (Carrillo, Laine et al. 2014).

	system I	system II
SDS	3.0	3.0
NaCl	2.7	2.7
water	67.7	78.2
limonene	8.0	8.0
n-pentanol	3.1	3.1
urea	12.5	
NaOH	3.0	
ethylenediamine		5.0

Figure 17 Composition of microemulsions (Carrillo, Laine et al. 2014).

The oven-dried pulps are introduced to the micro-emulsions at 3% solid and left for twelve hours at ambient temperature. The treated fibers are then washed and filtered by deionized water. Finally, the treated fibers were homogenized at different pressures and amounts or passes in order to generate nanofilament. The characterization of nanofilaments form AFM shows that the treated pulp from urea-containing microemulsion delivers fine filaments and contain less bundles as shown in Figure 18 (Carrillo, Laine et al. 2014).

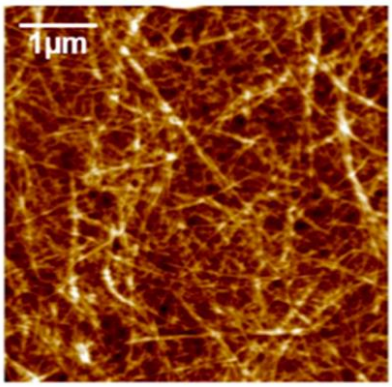


Figure 18 Treated fiber from urea-containing microemulsion and mechanical treatment (Carrillo, Laine et al. 2014).

Carillo et al., 2013 also investigates the optimal formulations of microemulsion by identifying the appropriate compositions in S-O-W systems. The proper combination improves the rate and amount of liquid penetration of cellulosic materials at room temperature and atmospheric pressure. Surfactant concentration and salinities in aqueous phase have been examined to obtain thermodynamically stable and transparent microemulsions. Increasing salinity causes higher viscosity and bigger drop size, resulting in less effective penetrating ability in lignocellulosic structure. The surfactant mixture also play an important role in fluid penetration. Mixed surfactant emulsions (based on lignosulfonate and SDS) illustrated in Figure 19 are more effective than single SDS (Sodium dodecylsulfate) systems (Carrillo, Saloni et al. 2013).

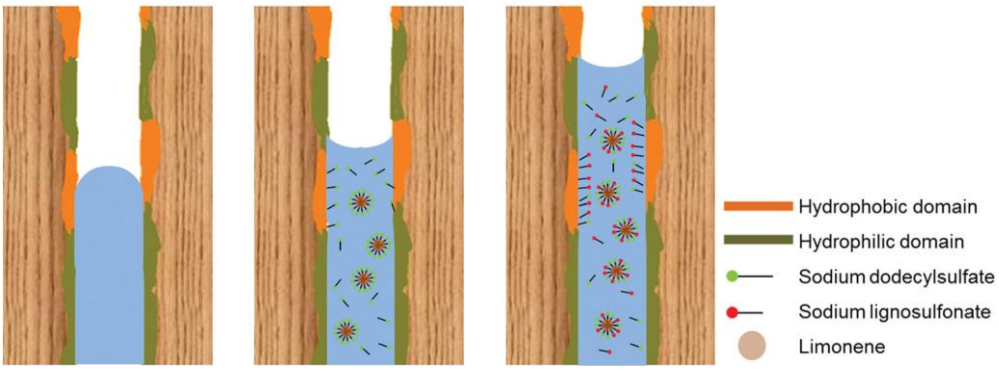


Figure 19 Fluid penetration of water, single system, and mixed surfactant system (Carrillo, Saloni et al. 2013).

2.4.6 Mechanical treatments (Microfluidization, Homogenization, HC refining)

Mechanical treatments are concerned as the major cost for production of CNF. As a consequence, many mechanical disintegrations have been examined to prepare the nanoscaled cellulose filaments. Usually, the mechanical treatments are used after pretreatment methods to separate single filament from a bundle of cellulose. The different mechanical treatments reflect the energy consumption in a particular method.

The homogenization process illustrates the most expensive and energy consuming methods for filament isolation. The major challenge of homogenization is the blocking problem in the instrument. Besides, the energy consumption of direct fibrillation without any pre-treatments requires larger energy consumption. As a consequence, pretreatments of cellulosic materials are important to perform in order to loosen the structure, decrease the size of cellulose and mitigate the fibrillation process. The common pretreatment methods could be chemical, or enzymatic methods in order to reduce energy consumption during the mechanical disintegration. The energy saving from pre-treatments may reach up to 98% after pre-treatments (Josset, Orsolini et al. 2014).

In 1998 (Josset, Orsolini et al. 2014), the first method used for fibrillation is grinding process. The principle of grinding is introducing the cellulosic materials to two ceramic stones. The rotating ceramic plate moves while the other plate acts as a stator. When the cellulose enters the channel with high speed, the fibrillation occurs as a result of high shearing forces happening between two ceramic plates. Usually, fibrillated cellulose is passed through the grinder many times until the final quality is reached. The advantages of this process is simple and effective. Furthermore, the chamber can contain large fibers without blocking. However grinding produces CNF with less homogeneous diameters compared to homogenizer. Moreover, the grinding process has been shown to cause fiber degradation due to the high shear forces between two grinding stones (Josset, Orsolini et al. 2014).

Ball milling method also used for producing nanofilament as well. It is possible to operate the ball milling in both wet and dry conditions. However, the wet ball milling is preferred because the liquid creates a buffer between cellulose particles and thus reduces the degradation of the cellulose crystallinity. The ball milling has been recently applied for disintegrating nanofilament by using water and organic solvents as milling media (Amin, Annamalai et al. 2015). The outcome from these ball milling techniques shown in Figure 20 generates the nanofibrillated and microfibrillted cellulose.

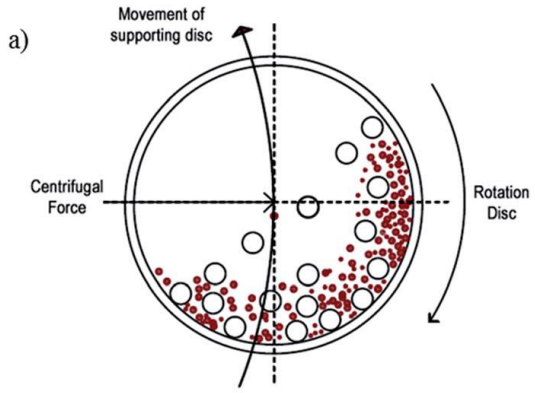


Figure 20 Ball milling method (Amin, Annamalai et al. 2015)

Joonobi et al. 2012 have studied the mechanical treatment of sludge, obtained solid waste and contain shorter fiber, from waste water treatment to produce nanofilament. Cellulose nanofilaments are successfully disintegrated from sludge pulp by using grinder since the process could possibly reduce the processing cost in terms of energy consumption and pre-treatment chemicals. The nanofilaments from sludge results in higher specific surface area than nanofilament from native cellulose. The physical properties of nanofilaments comprise high network density, excellent tensile strength, and transparent materials. Moreover, the thermal stability of quite similar to the original cellulose. All in all, this treatment shows ease of fibrillation and lower energy consumption as well as results in comparative properties as native cellulose (Jonoobi, Mathew et al. 2012).

Ultrasonication is another mechanical treatment used for producing cellulose filament. The principle of this technique is the application of sound energy to create high-speed liquid jets. The velocity of pressurized liquids is approximately 1000 km/h and

subsequently promotes separation of fibrillation, collision and degradation of polysaccharide linkages as shown in Figure 21 (Li, Yue et al. 2012, Amin, Annamalai et al. 2015).

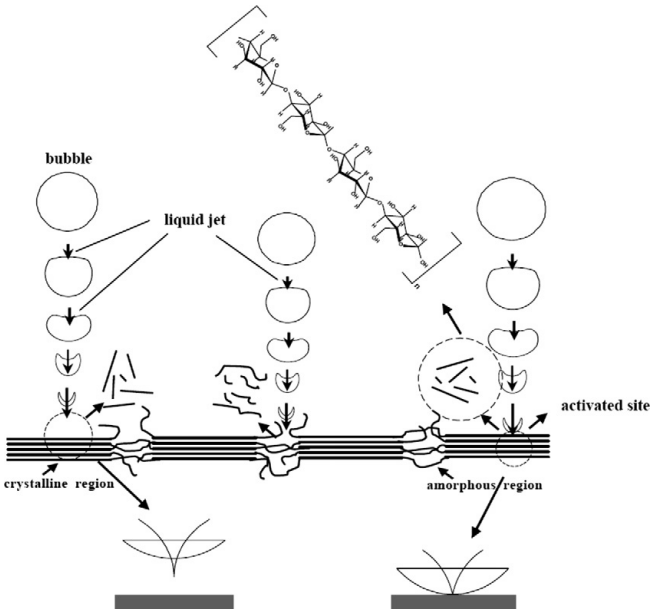


Figure 21 Working principle of the ultrasonication technique (Li, Yue et al. 2012, Amin, Annamalai et al. 2015)

The jets non-selectively collide the surface of cellulose with enormous force caused serious damages at the impact point and yield highly reactive surfaces. However, the crystallinity of cellulose may reduce from this treatment about 11% (Li, Yue et al. 2012) and also the length of nano filaments are shorter after the prolonged exposure to ultrasonication as shown in TEM images from Figure 22.

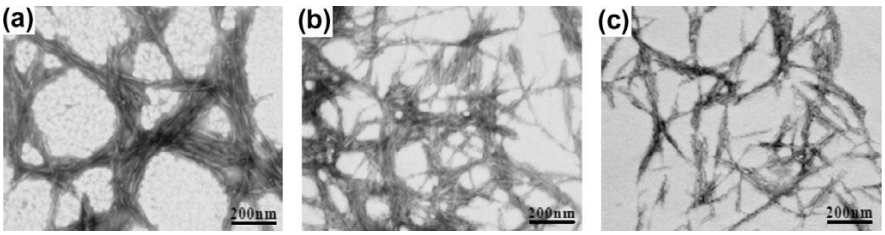


Figure 22 TEM images of nanocrystalline cellulose at different ultrasonication time a) 5 minutes b) 10 minutes and c) 15 minutes

Mechanical treatments are one of the most energy requirement to produce CNF at an industrial scale. The study from Spence et al. 2011 compared the production cost of CNF from different methods (homogenization, microfluidization, micro-grinder). The homogenizer yielded the better in mechanical properties and higher specific area with lower water vapor transmission. Moreover, the production cost (Figure 23) of CNF from recycled fiber is significantly lower than those produced from wood (Spence, Venditti et al. 2011).

Material	Process	Energy cost per ton	Energy & material cost per ton	Material	Market price per ton
Bleached hardwood (BHW)	Homogenizer 8 Pass + Pre	$650	$1,300	LDPE*	$1,500
	Microfluidizer 5 Pass + Pre	$140	$790	HDPE*	$1,400
	Micro-grinder 9 Pass + Pre	$210	$860	PP*	$1,840
	Micro-grinder 9 Pass	$95	$745	PS*	$1,600
	Homogenizer 20 Pass	$1,310	$1,960	PLA**	$1,900
Unbleached hardwood (UBHW)	Homogenizer 8 Pass + Pre	$650	$1,000		
	Microfluidizer 5 Pass + Pre	$140	$490		
	Micro-grinder 9 Pass + Pre	$210	$560		
	Micro-grinder 9 Pass	$95	$445		
	Homogenizer 20 Pass	$1,310	$1,660		
Recycled fiber	Micro-grinder 9 Pass	$95	$195		
Sludge	Micro-grinder 9 Pass	$95	$115		

Figure 23 Cost comparison between CNF produced from wood-based fiber and recycled fiber from different methods

2.5 Further processing and potential applications of CNF

2.5.1 Filament spinning from recycled CNF

CNFs have been successfully spun into continuous filaments from solely native cellulose (Hooshmand, Aitomäki et al. 2015). Hooshmand et al. 2015 have examined dry-spun filaments from cellulose nanofibers produced from banana rachis. The CNFs have been deconstructed with Masuko ultra-grinder to obtain a gel-like viscous slurry. After that, concentration of the slurry has been increased to 8, 10, 12% concentration and subsequently dry-spun with different rates. The filaments show excellent mechanical properties from lower concentration with high spinning rate. The SEM also confirms that a densed filament structure as shown in Figure 24 (Hooshmand, Aitomäki et al. 2015).

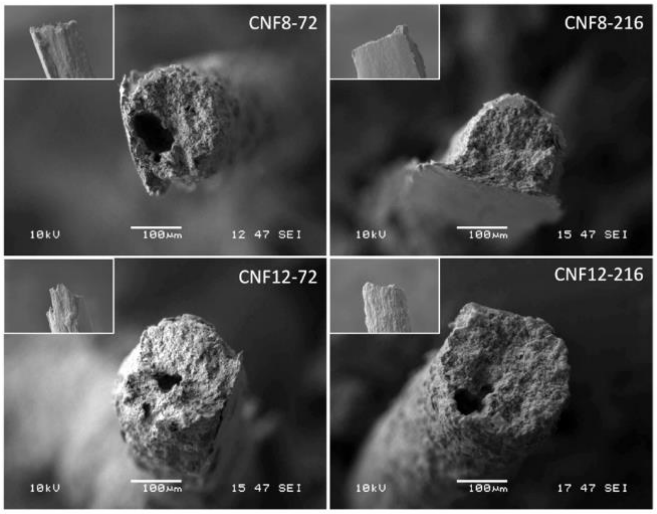


Figure 24 SEM micrographs of filaments at 8 (top) and 12% (bottom) concentration spun at 72 (left), 216 (right) mms^{-1} (Hooshmand, Aitomäki et al. 2015)

The filaments have a modulus of approximately 10 GPa, which is lower than natural fibers (40 GPa). However, the mechanical strength of filaments is comparable to regenerated cellulose filament (11 GPa) and the CNF are obtained from waste biomass without additives. Thus, this method can be further developed by optimization of the process parameters and application of additives and/or functionalizations (Hooshmand, Aitomäki et al. 2015).

2.5.2 Applications of CNF in papermaking

CNFs are applied in papermaking as retention aids as well as also strength reinforcement. For the retention aids application, cellulose filament is directly added to precipitated calcium carbonate (PCC) slurry before adding to pulp furnish. After that, cationic starch is also mixed for wet strength agent. First part retention (FPR) and first part ash retention (FPAR) are dramatically improved from 54% to 84% and 18% to 73%, respectively, for the absent of retention aids in wet-end system as illustrated in Figure 25. For the presence of retention aid chemicals, the FPR and FPAR are enhanced as well from 74% to 93% and 53% to 89% respectively. Thus, it is clear that the fibrils improve wet-end system in papermaking by collecting fillers, fines, and chemicals and also subsequently results in good runnability of paper machines (Hua, 2011).

Furnish	Retention aid chemicals	FPR, %	FPAR, %
Pulp + 50% PCC + 14 kg starch	No	54	18
Pulp + 50% PCC + 14 kg starch	0.5 kg CPAM + 0.3 kg S/0.3 kg MP	74	53
Pulp + (50% PCC + 5% CNF) + 14 kg starch	No	84	73
Pulp + (50% PCC + 5% CNF) + 14 kg starch	0.5 kg CPAM + 0.3 kg S/0.3 kg MP	93	89

Figure 25 Benefit of cellulose filament on the FPR and FPAR in wet-end application (Hua, 2011)

CNF can be applied as a wet strength agent in web-forming as well. The dosage of cellulose filament is quite low: only 0.8% by weight as shown in Figure 26. Wet strength, dry strength, and cationic starch are used and compared the performance against cellulose filament. As a result, the tensile energy absorption (TEA) index improves at 72% compared to control while the other chemicals are failed enhancing the wet web (Hua, 2011).

Additive	Dosage (%)	TEA index (mJ/g)
Control	0	33
CNF	0.8	57
Wet strength resin	0.8	31
Dry strength resin	0.8	32
Cationic Starch	2	33

Figure 26 Strength enhancement of CNF compared with wet strength resin, dry strength agent, and cationic starch (Hua, 2011)

2.5.3 Applications of CNF in composite materials

Nanofibers have been used as a reinforcement in composite last fifteen years ago as shown in Figure 27 (Eichhorn, Dufresne et al. 2010). Since the modulus of crystalline cellulose is as high as steel, many researches have been utilized nanofibers as a reinforcement in composites.

Material	Modulus (GPa)	Density (Mg m^{-3})	Specific modulus (GPa Mg^{-1} m^3)
Aluminium	69	2.7	26
Steel	200	7.8	26
Glass	69	2.5	28
Crystalline cellulose	138	1.5	92

Figure 27 Modulus of cellulose compared to engineering materials (Eichhorn, Dufresne et al. 2010).

The main advantage of utilizing cellulose nanofibril is the mechanical strength. The mechanical prediction of composite materials could be adopted by Halpin-Tsai micromechanical prediction as shown in Figure 28. The principle of this theory is based on the assumption that the constituent properties and the fraction volume of two phases (reinforcement and matrix) are known. Then, the elastic constant of composites could be predicted as a function of different fiber aspect ratio. From the study in Figure 28, the high aspect ratio of nanofilament is beneficial to reinforcement effect in composites. For the low aspect ratio smaller than 10, there is no significant

benefits to composites compared to the original macroscopic cellulose. The aspect ratio of nanofilament larger than 50, the effective reinforcement could be visibly observed. Finally, the higher aspect ratio more than 100 yields the upper-limit reinforcement where the Young's moduli reached a plateau level.

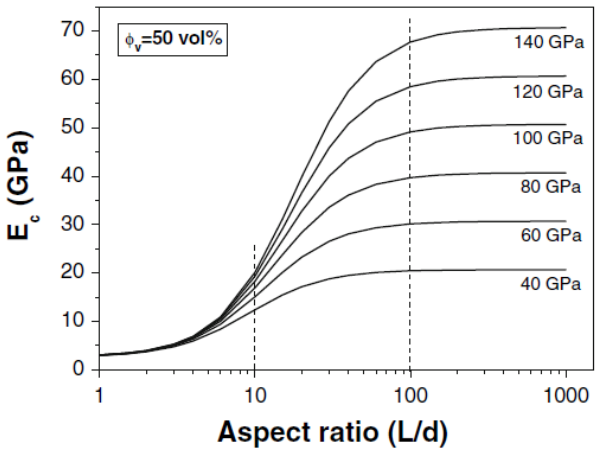


Figure 28 The Halpin-Tsai model illustrating the composite modulus (E_c) as a function of the aspect ratio of the nanofiber reinforcement

From the study of Hua (2011), cellulose nanofibers are utilized as reinforcement in composite materials. The result shown in Figure 29 illustrates that cellulose filament is the best matrix reinforcing the composite structure. The tensile index and elastic modulus of nanocomposite films are significantly improved from the control.

Tensile strength of nanocomposite reinforced with nanofilaments

Matrix	CNF (%)	Tensile index (N · m/g)	Elastic modulus (km)
Styrene-butadiene copolymer	0	2.06	3.0
Styrene-butadiene copolymer	7.5	7.26	50
Carboxy methyl cellulose	0	49.7	521
Carboxy methyl cellulose	7.5	63.5	685

Figure 29 CNF as matrices in nanocomposite films

In this thesis, the recycled pulp is treated with two pretreatment techniques (TEMPO-oxidation at two oxidation levels, and carboxymethylation) in order to introduce carboxylic groups with negative charges. The mechanical disintegration will be carried out with homogenization and microfluidization to produce CNF. Then, the CNF, as intermediate, will be applied in two applications: filament forming in textile application and strength additives in papermaking. The potential of two applications will be discussed and the recommendation for future research will be addressed as well.

Chapter 3. Materials and methods

This chapter explains the materials and methods to fabricate the cellulose filament and additives in papermaking. Characterization techniques and testing methods are also mentioned in order to evaluate the mechanical properties of the cellulose filaments and the papers. Sections 3.1 describes the materials and instruments used in filament forming and additives in paper. Section 3.2 discusses the procedures, and conditions for conducting laboratories.

3.1 Materials

3.1.1 Waste cardboard and stock pulp

Recycled fiber was obtained from disintegration of corrugated board from IKEA as shown in Figure 30. The procedure of wet disintegration was used to obtain recycled pulp. The recycled pulp was stored in cold room at 4^{o}C for further experiments.

Figure 30 IKEA cardboard as raw material

The amount of 10 kg of stock pulp was received from Pankaboard. The stock pulp had the consistency of 1.93% and contain no bentonite, calcium carbonate, and other additives. The freeness of stock pulp was approximately 350 CFS.

3.1.2 Chemicals

2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) used in this study was manufactured by Sigma-Aldrich and Sodium Bromide (NaBr) at 99% was produced from Riedel-de Haen. Sodium hypochlorite (NaClO) was purchased from VWR and

diluted to 13 %w/v before use. Hydrochloric acid with concentration 1 M and 0.1 M were manufactured by Titripur. Pellet of Sodium chloride and Sodium hydroxide were also manufactured by VWR. Acetone with > 99% was purchased from Sigma-Aldrich while the ethanol with 99.5% was manufactured by ETAX. Glacial acetic acid >99.85%, isopropanol > 99.5%, Sodium chloroacetate 98%, and PVA with average M_w 25000 in powder were manufactured by Sigma-Aldrich. Deionized water was used for every experiment in this thesis.

3.2 Methods

3.2.1 Disintegrating corrugated board into pulp slurry

Corrugated board from IKEA used to contain furniture was disintegrated into pulp slurry. According to **ES ISO 5263-1:2012,** the corrugated board was soaked in water overnight to assure that the paper was fully saturated and disintegrate into pulp slurry. The soaked paper was introduced to the pulper approximately 100-200 g (wet weight) each time and carried out with 30000 revolutions. A small sample of disintegrated pulp was immediately observed by diluting with water in a glass cylinder and evaluate whether it was completely isolated.

Thereafter, flat screen or Mänttä was located in Puu2 used for screening large contaminants from pulp slurry, i.e., macrostikies, fiber bundles, plastic film, and metal. There are many size for the slot of the screening plate. In this thesis, the 0.17 mm slot was used to classify the recycled fiber from contaminants. The recycled pulp was constantly introduced to the screen 300 ml each time to avoid the clog of screen.

3.2.2 Pretreatments of recycled fiber

Two pretreatment techniques were used to modify surface charges of recycled fiber: TEMPO-oxidation and carboxymethylation. The TEMPO-oxidation was applied with two levels of oxidation while the carboxymethylation was carried out on one level only.

- *Pretreatment with TEMPO at low oxidation level (TO_low)*

The solution between TEMPO and NaBr was prepared by dissolving TEMPO 0.091 g and NaBr 2.153 g in 370 ml of deionized water. Then, 4.5 gBD of pulp slurry

was mixed with the TEMPO + NaBr solution. After that, 2.42 mmol/g of NaClO 13 was introduced to pulp slurry and maintain the pH at 10.5 with 1 M NaOH. If there was no NaOH consumption, the oxidation reaction was believed to complete. Finally, the pH of pulp slurry was adjusted to pH 7 with 1M HCl and follow by filtration until the conductivity of filtrate decreased below 5 µS/cm. The washed pulp was stored at 4°C for further analysis.

- *Pretreatment with TEMPO at high oxidation level (TO_high)*

The procedure in this pretreatment was similar to those in TO_low except the quantities of chemicals. The solution between TEMPO and NaBr was prepared by dissolving TEMPO 0.182 g and NaBr 4.306 g in 740 ml of DI water. Then, 4.5 gBD of pulp slurry was mixed with the TEMPO + NaBr solution. After that, 5 mmol/g of NaClO 13% was introduced to pulp slurry and maintain the pH at 10.5 with 1 M NaOH and washing as mentioned in the previous treatment.

- *Pretreatment of recycled fiber with carboxymethylation method (Car)*

The pulp slurry with 7 gBD was mixed with NaOH 1 g, Sodium Chloroacetate 1.485 g and make up the total volume to 500 ml with deionized water. The slurry was left for 1 hour with magnetic stirring. Then, the pulp was washed three times with three solutions. The first solution was introduced to the pulp with the mixture of 100 ml of 0.05 M acetic acid and 100 ml of 5/3 v/v isopropanol/ ethanol and centrifuged at 4500 rpm for 45 minutes at 25°C. After that, the supernatant was removed after the centrifugation. The second washing, the washed pulp was immersed the mixture of 100 ml 0.05 M NaOH and 100 ml 5/3 v/v isopropanol/ ethanol and then centrifuged at 4500 rpm for 45 minutes 25°C. The supernatant was also removed after the centrifugation. Finally, the pulp was washed again with the mixture of 100 ml of deionized water and 100 ml of 5/3 v/v isopropanol/ ethanol with centrifuge at 4500 rpm for 45 minutes at 25°C. Then, the supernatant was removed accordingly.

3.2.3 Evaluation of total carboxylic groups

The number of acidic (carboxylic) groups was evaluated by conductometric titration (shown in Figure 31) and following the SCAN-CM 65:02. The pretreated pulps were

pretreated by protonization in 0.1 M HCl for 15 minutes at 1% consistency and washed by filtration method until the conductivity of the filtrate decreased below 5 µS/cm. Before conductometric titration, CO_2 in Milli-Q water was removed by suction 1-2 hours before titration. One gram of protonated fiber was taken and added 500 ml of CO_2-free water, 0.5 ml of 0.5 M NaCl, 1 ml of 0.1 M HCl all together. Then, started the mixing with magnetic stirrer and placed the lid over the beaker with paraffin film to prevent CO_2 entering from air. After conductometric titration, the graph was extrapolated to obtain the total amount of acidic groups. The first region, the conductivity of the solution decreased rapidly from neutralization of protonated carboxylic groups of pulp with OH^- ion from the adding titrant. The second region, a slight reduction in conductivity (plateau region) was observed due to neutralization of the protons liberated by the salt. The conductivity remained unchanged, since the Na^+ was adsorbed as counter-ions to the carboxylic groups, the dissociated H^+ was completely neutralized by adding OH^-. The last region, the conductivity increased due to the excess of OH^- ions in the solution. The carboxylic groups content were calculated from the strong and weak acid regions as shown in equation 1.

$$X = \frac{C_t V_2}{m}, \qquad (1)$$

Where X is the total acidic group content (mmol/g), C_t is the concentration of the sodium hydroxide solution (mmol/l), V_2 is the volume of the sodium hydroxide solution consumed during the plateau region in the conductivity (L) and m is the oven-dry weight of sample (g)

Figure 31 Conductometric titration

3.2.4 Fibrillation of pretreated recycled fiber

The pretreated recycled fibers were disintegrated into CNF by two mechanical treatments. First, the treated fibers were diluted to 2% consistency with deionized water and adjusted the pH to 9-10 for good swelling. The homogenizer was use to disintegrate the fibrils in cellulosic fibers with high-shear force in order to obtain the homogeneous slurry. The mechanical disintegration used for defibrillating the pretreated recycled fiber were homogenized at 12000 rpm for 5 minutes with the Ultra-Turrax IKA T25 digital homogenizer. Every one minute, the homogenizer was stopped for 30 seconds to avoid heat accumulation in the pulp slurry. After that, the homogenized slurries were isolated into CNF with the microfluidizer for three passes. The size of the chamber was 100 and 200 µm and operated under 2000 bars.

3.2.5 Filament forming from wet spinning

The microfluidized-homogenized TEMPO at high oxidation level (M-H-TO_high) was used to spin continuous filaments. The centrifugation technique was used to increase solid content of the sample up to 2% solid. After that, the sample was introduced to the metal syringe (internal diameter 2 cm) which was attached to a syringe (needle size 0.5 mm). The spinning rate was 1 ml/min for every samples and the coagulation bath was acetone. Spin filaments were collected from the bath and dried under a small tension for 15 minutes. The ratio of M-H-TO_high and additives were illustrated in Table 1. The 100% CNF (TOCNF with 6 passess were obtained from Biobased Colloids and Materials group) produced from virgin was also spun and compared with CNF produced from recycled fiber.

Table 1 Ratio of M-H-TO_high and additives for filament forming

	M-H-TEMPO high (gBD)	**Additives (gBD)**
100% M-H-TO_high from recycled fiber	4	0
100% CNF from virgin fiber	4	0

90% M-H- TO_high + PVA 10%	4	0.4
90% M-H- TO_high + CNF (virgin) 10%	4	0.4

3.2.6 Paper formation

Handsheets for physical testing were made according to ISO 5269-1: 2005 Pulps -- Preparation of laboratory sheets for physical testing -- Part 1: Conventional sheet-former method. The handsheet mold is located in sheet-making room, Puu2, Aalto University. The stock pulp had the consistency of 1.93% and did not contain bentonite, calcium carbonate, and other additives. The stock pulps were mixed with four different additives: Homogenized TEMPO-oxidized recycled fiber at low oxidation level (H-TO_low), Microfluidized-Homogenized TEMPO-oxidized recycled fiber at high oxidation level (M-H-TO_high), and Microfluidized-Homogenized Carboxymethylated recycled fiber (M-H-Car). Then, the mixture of pulp and additives were dilute with deionized water in order to obtain 0.5% consistency. Finally, the diluted pulp slurries were used for making 80 gsm handsheets. The ratio of pulp, additives, and water were presented in Table 2.

Table 2 Ratio of pulp, water, and additives for handsheet forming

	Pulp (gBD)	**Water (ml)**	**Additives (gBD)**
Control	8.712	1291	0
25% H-TO_low	5.994	1291	2.178
25% M-H-TO_high	5.994	1291	2.178
25% M-H-Car	5.994	1291	2.178

Note: The ratios presented above are based on four handsheets per batch

3.2.7 Mechanical testing of cellulose filament

All filaments were tested according to ISO 5079:1995 Textile fibers -Determination of breaking force and elongation at break of individual fibers. The Vibrodyn 400 model

shown in Figure 32 was used to determine the tension of a single filament as a function of elongation in both dry and wet condition. The gauge length was 20 mm and speed 20 mm/ min. Titer (mass density of fiber), Force, Elongation, and tenacity (tensile) of filaments were determined after conditioned at 23°C, 50% RH for a night. Ten filaments per sample were tested and statistically calculated for further comparison.

Figure 32 Vibrodyn 400 for strength measurement of filaments

3.2.8 Paper properties testing

The handsheets were conditioned according to T402 sp-08 at 50% RH and temperature 23°C before physical testing,

Strength properties

- Thickness of handsheets were determined by following the ISO 534 Paper and Board – Determination of thickness, density and specific volume.
- Roughness was characterized by ISO 8791-2 Paper and board – Determination of roughness/ smoothness (air leak methods) – Part2: Bendtsen method while the porosity was measured according to the ISO 5636-3 Paper and board – Determination of air permeability (medium range) – Part3: Bendtsen method.
- Tensile strength, Tensile Energy Absorption, and Tensile Stiffness were measured according to the ISO 1924-2:2008 - Paper and board - determination of tensile properties - Part 2,3 : Constant rate of elongation method (20, 100 mm/min) with L&W ALWETRON TH1 tensile tester in paper testing room, PUU1 laboratory, Aalto University.
- Load Elongations of papers were examined with MTS 400 Tensile tester located in paper testing room, Puu1, Aalto University as shown in Figure 33.

After 4 hours of conditioning, papers were cut in 15 mm in width for 10 pieces and tested following ISO 1924-2: 2008 Paper and board -- Determination of tensile properties -- Part 2: Constant rate of elongation method (20 mm/min).

Figure 33 MTS 400 for measuring load elongation of papers

Surface properties

- Surface roughness was measured by following the ISO 8791-2- Determination of roughness/smoothness (air leak methods) - Part 2: Bendtsen method by L&W Bendsten tester, Paper testing room, PUU1 laboratory, Aalto University.

Structural properties

- Thickness of paper was measured according to ISO 534:2011 Paper and board - Determination of thickness, density and specific volume by L&W micrometer in paper testing room, PUU1 laboratory, Aalto University.

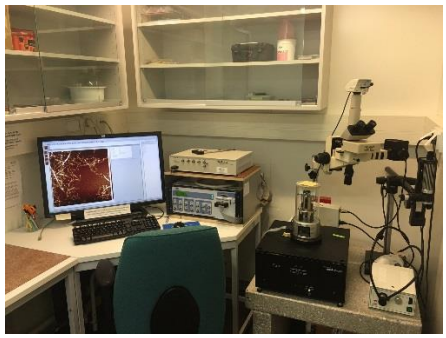
3.2.9 Characterization of functional groups

Fourier Transform Infrared Spectroscopy

- Functional groups in cellulose were identified with Fourier Transform Infrared Spectrometer at laboratory in Nanotalo, Department of Applied Physics, Aalto University. All of the samples were oven dried before characterization with FTIR to avoid disturbance from water molecules.

3.2.10 Surface topography with Scanning Electron Microscope (SEM) and AFM

- Scanning Electron Microscope (SEM) was used to characterize the surface topography located in the Nanotalo, Department of Applied Physics, Aalto University as shown in Figure 34 a. Small pieces of samples were placed on double-taped stubs and spluttered with platinum to generate conductive surface and higher resolution.



a) **b)**

Figure 34 a) Scanning Electron Microscope b) Atomic Force Microscope

- Atomic Force Microscopy (AFM), shown in Figure 35 b, was used to obtain high resolution images of nanofibrils and located in PUU1 laboratory, Aalto University. The tapping mode was used to construct images under supervision of specialist.

3.2.11 Fiber length analysis

The Kaajani FS-200 Fiber analyzer located in fiber lab, PUU1 laboratory, Aalto University, was used to characterize fiber length (mm), %fines, and fiber curl.

Chapter 4. Results and Discussion

This chapter discusses the laboratory results. Section 4.1 describes the results from the four characterization methods to indicate the presence of carboxylic groups in recycled fibers. The results from modifying recycled fiber are presented in Section 4.2. Section 4.3 and 4.4 explain about two applications of nanofibrils in textiles and papermaking.

4.1 Pretreatments of recycled fiber with TEMPO oxidation and Carboxymethylation

The TEMPO-pretreated recycled fiber was characterized using three techniques described in Sections 4.1.1-4.1.3 in order to qualitatively and quantitatively identify the presence of carboxylic groups. Section 4.1.4 explains about the fiber length analysis of untreated and treated recycled fibers.

4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The TEMPO-treated recycled fiber was analyzed with a spectroscopic technique for detecting carboxylic group at the surface of the fiber. Before characterizing the sample with FTIR, it must be dried in order to avoid disturbance by the strong, broad spectrum of O-H from water molecules (3600-3200 cm^{-1}).

The FTIR spectroscopic results are shown in Figure 35. The figure clearly demonstrates that the carboxylic groups are qualitatively identified with sharp peak at 1760-1690 cm^{-1}, as was earlier observed by Saito et al. (2006). Three samples: TEMPO-oxidized recycled fiber at low oxidation level (TO_low), TEMPO-oxidized recycled fiber at high oxidation level (TO_high), and carboxymethylation of recycled fiber (Car), were successfully introduced carboxylic groups at the surface of fibers. Additionally, a large band between 2950-2850 cm^{-1} with C-H stretching were observed for the carboxymethylated recycled fiber due to the presence of methyl groups ($-CH_3$). This FTIR result also agrees with the finding of Eyholzer et al. 2010. In addition, the subsequent mechanical disintegration has no effect and change in the FTIR spectrum (Eyholzer, Bordeanu et al. 2010).

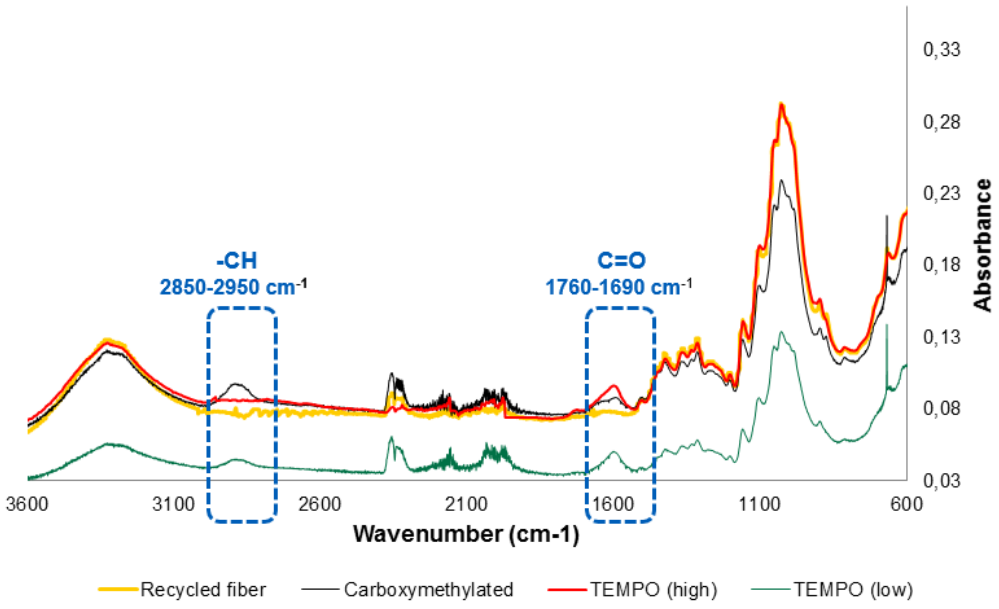
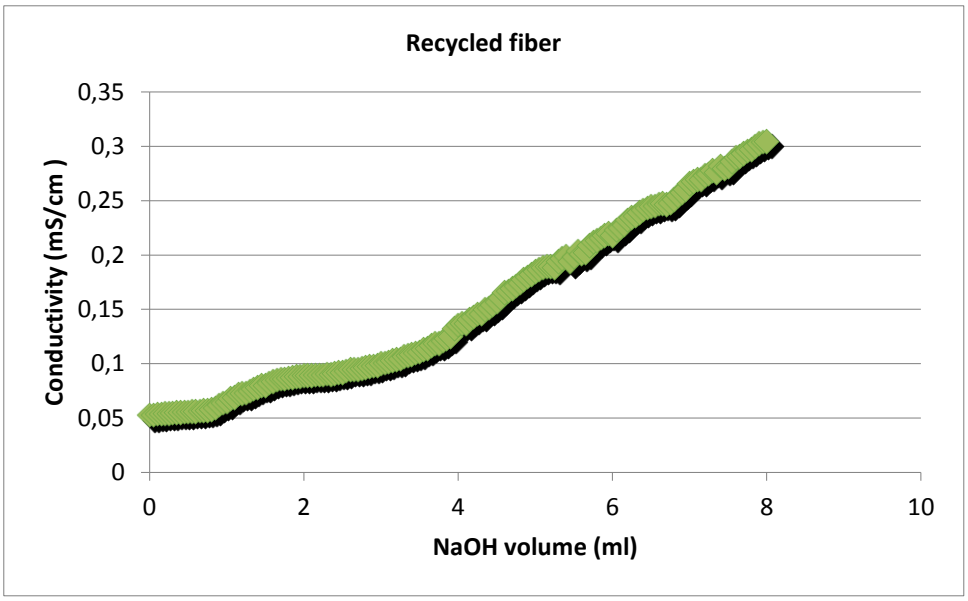


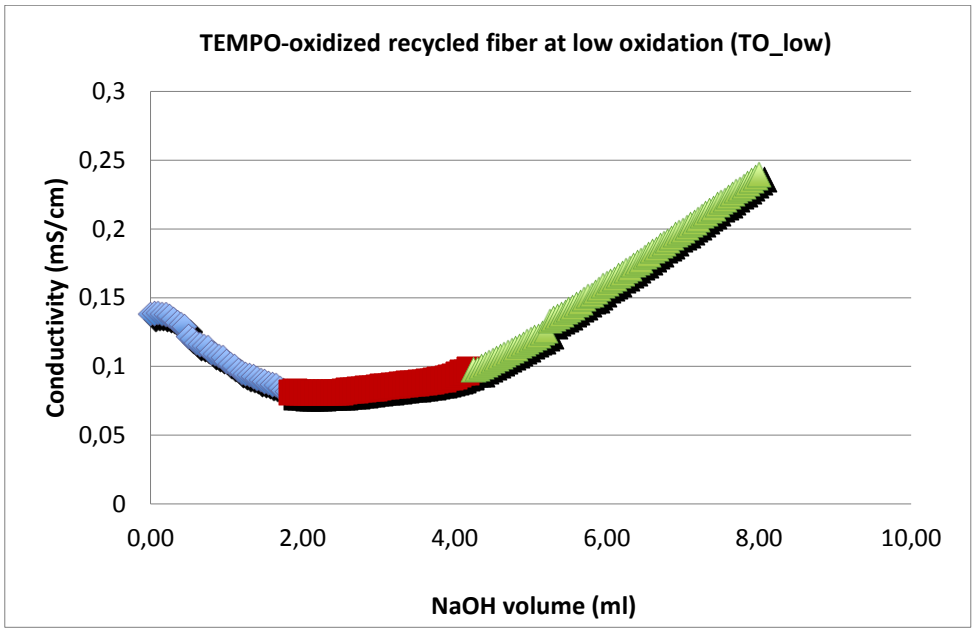
Figure 35 FTIR spectra of TEMPO-oxidized recycled fiber with carboxylic groups (C=O) stretching at 1726 and 1700 cm^{-1}.

4.1.2 Conductometric Titration

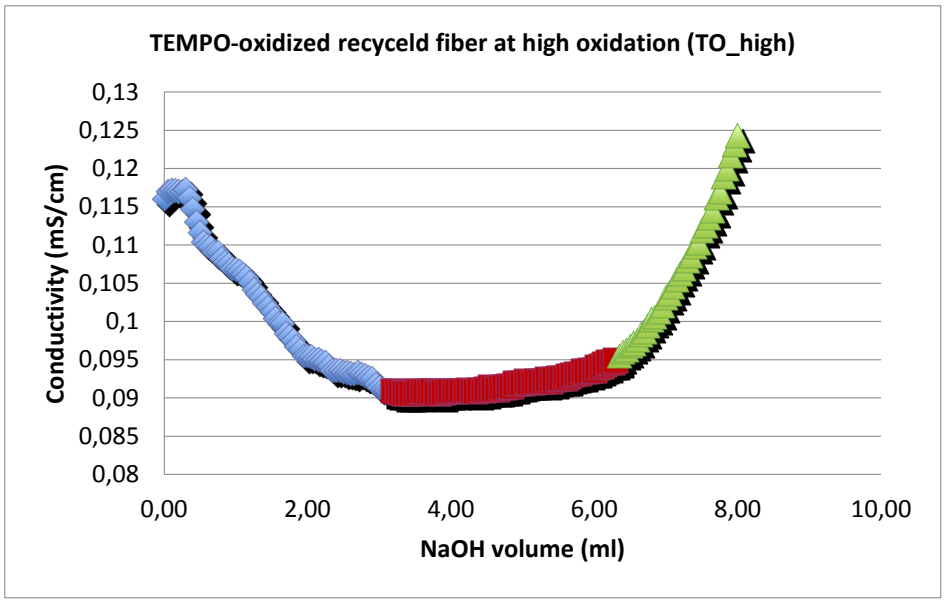
The amount of carboxylic groups were quantitatively measured with conductometric titration. The graph represents the conductometric titration curve of TEMPO-oxidized recycled fiber, which the conductivity was plotted versus the amount of NaOH added. The conductivity was high at the beginning because of the conductivity of protonated carboxylic groups in pulp. Once NaOH was added, the conductivity started decreasing due to the neutralization of hydronium ions in protonated carboxylic groups by added OH^- from the titrant. The conductivity continued decreasing until the equivalence point (plateau region), which there were only NaCl molecules in the solution. After that, the conductivity improved due to the excess amount of OH^- ions adding from the titrant. From this point, it can be inferred that the sample pulp does not contain positive acid groups anymore. All of the conductometric titration curves were presented in Figure 36 a) to d).


Recycled fiber
Conductivity (mS/cm)
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
2
4
6
8
10
NaOH volume (ml)

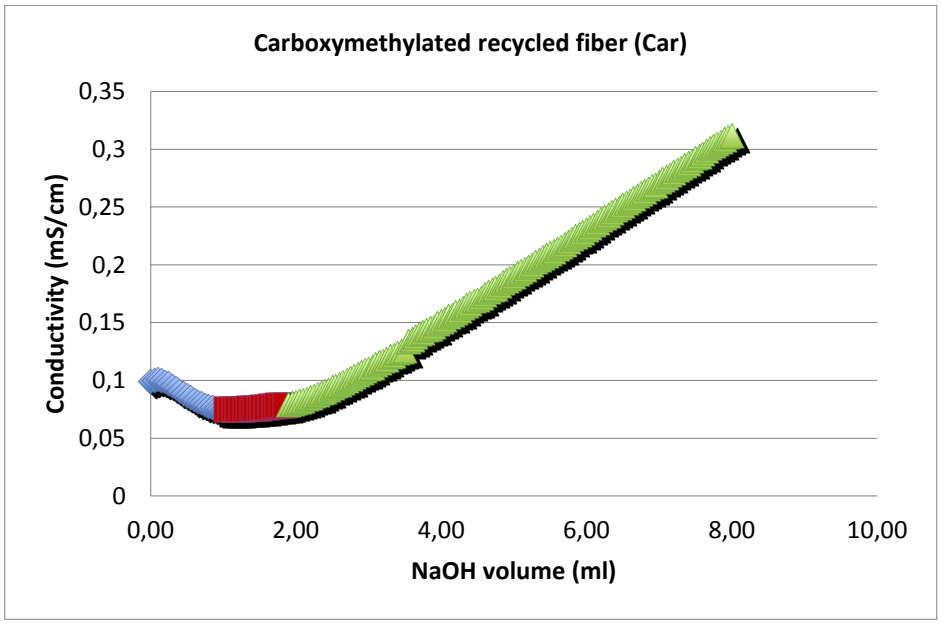
a)


TEMPO-oxidized recycled fiber at low oxidation (TO_low)
Conductivity (mS/cm)
0,3
0,25
0,2
0,15
0,1
0,05
0
0,00
2,00
4,00
6,00
8,00
10,00
NaOH volume (ml)

b)



c)



d)

Figure 36 Conductometric titration curve of a) recycled fiber (untreated) b) TEMPO-oxidized recycled fiber at low oxidation level (TO_low), c) TEMPO-oxidized recycled fiber at high oxidation level (TO_high), and d) carboxymethylation of recycled fiber (Car)

In order to determine the behavior of the conductivity in TO recycled fiber, the curve was divided into three regions corresponding to the level of conductivity found in the sample.

Region 1 (Blue): the conductivity of the solution decreased rapidly from neutralization of hydronium ions in the solution as well as strong acidic groups with OH^- ion from the adding titrant. After complete neutralization of the strong acid groups, a slight reduction in conductivity was observed due to neutralization of the protons liberated by the salt.
Region 2 (Red): the conductivity remained unchanged, since the Na^+ was adsorbed as counter-ions to the carboxylic groups, the dissociated protons was completely neutralized by adding OH^-.
Region 3 (Green): the conductivity increased due to the excess of OH^- ions in the solution.

The TEMPO-oxidized recycled fiber at low oxidation level (TO_low) contained the carboxylic content of 0.42 mmol/g. In addition, there were two other treated recycled fibers: TEMPO-oxidized recycled fiber at high oxidation level (TO_high) and carboxymethylation of recycled fiber (Car). The carboxylic-groups content of all samples were calculated and presented as shown in Table 3.

Table 3 Summary of carboxylic-groups content of all samples

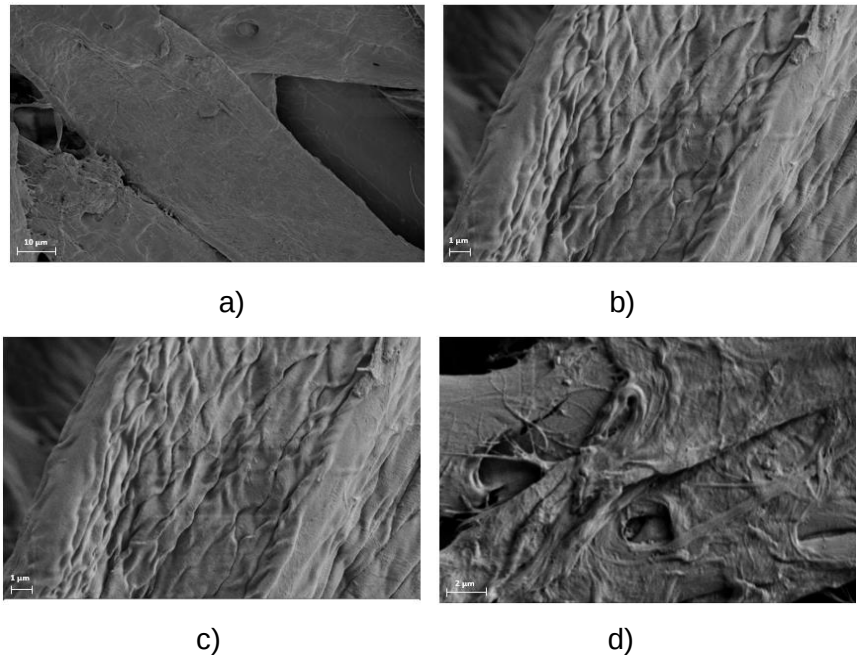
	NaOH volume (ml)	**Mass of fiber** (gBD)	**Carboxylic groups content** (mmol/g)
Control (untreated)	0.00	1	0.00
TO_low	4.2	1	0.42
TO_high	6.3	1	0.63
Car	1.85	1	0.19

The carboxylic group content with the amount of 0.42 mmol/g was found in the TEMPO-oxidized recycled fiber after the pretreatment. The conductometric titration

showed that the oxidation of recycled fiber introduced less carboxylic groups than those of native cellulose reported previously by Isogai (Isogai, Saito et al. 2011). The earlier studies, the hardwood bleached kraft pulp with carboxylic content of 0.8 mmol/g was obtained from the TEMPO-oxidation technique. This can be explained that recycled fiber exhibits reduced water accessibility, and less swelling compared to virgin fiber (Saito, Kimura et al. 2007).

4.1.3 Scanning Electron Microscope (SEM)

Morphological changes of unmodified, TEMPO-oxidized, and carboxymethylated pulp were observed with SEM to examine surface of cellulose. As shown in Figure 37, the structure of TEMPO-oxidized and carboxymethylated recycled fiber were maintained after modification with TEMPO (Saito, Nishiyama et al. 2006) and carboxymethylation. Furthermore, the oxidation with TEMPO was performed in mild enough conditions to preserve the fibrillar morphology and crystallinity in the recycled fiber even in higher oxidation level. The oxidation occurred only on the surfaces of fibers so there was no significant change in morphology of fibers as reported earlier by Saito (Saito, Kimura et al. 2007). In addition, there were the wrinkles at the surface of fibers due to the hornification effect of recycled fibers.



a) b)

c) d)

Figure 37 SEM images of a) untreated recycled fiber b) TEMPO-oxidized recycled fiber at low oxidation level (TO_low), b) TEMPO-oxidized recycled fiber at high oxidation level (TO_high), and c) Carboxymethylation of recycled fiber (Car)

4.1.4 Fiber length analysis

The fiber length analysis, as shown in Table 4, was carried out for untreated and treated samples in order to observe the distribution of fiber and morphological change. The average fiber length of untreated recycled fiber and treated fibers were maintained after pretreatment with both TEMPO and carboxymethylation. Additionally, the fine content in every sample was not much changed due to absence of mechanical disintegration during pretreatments. However, the average fiber length of TEMPO-oxidized recycled fiber at low oxidation level (TO_low) was slightly longer than other samples. Furthermore, the fines content of TO_low was also slightly lower than others. However, the error may originate from the poor sampling of fiber.

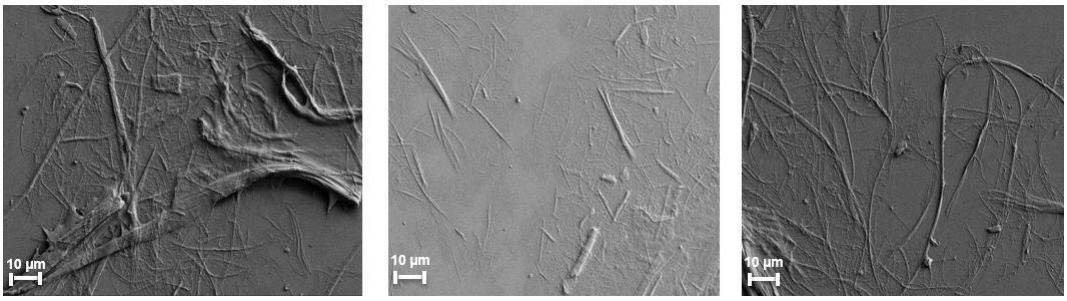
Table 4 Fiber length analysis of untreated recycled fiber and treated recycled fiber

Sample	Average fiber length (mm)	Fiber width (μm)	% Fines
Recycled fiber	0.66	20.14	25.99
TO_low	0.76	20.07	17.46
TO_high	0.69	20.13	21.50
Car	0.68	19.71	24.02

4.2 Fibrillation of pretreated fiber

Pulp slurry after pretreatments were homogenized with Ultra Turrax Homogenizer for 5 minutes at 12000 rpm. The slurry after homogenization exhibited more homogeneous, and slightly viscous. The carboxymethylated recycled fiber with carboxylate content 0.19 mmol/g required more energy during homogenization which is related to the earlier study by Naderi et al. 2015 (Naderi, Lindström et al. 2015). This result is comparable to those reported by Khalil et al. 2014 previously that the carboxylic groups facilitate defibrillation and prevent the blockage of homogenizer. The TEMPO-oxidized pulp with carboxylic content 0.3 mmol/g has obviously passed

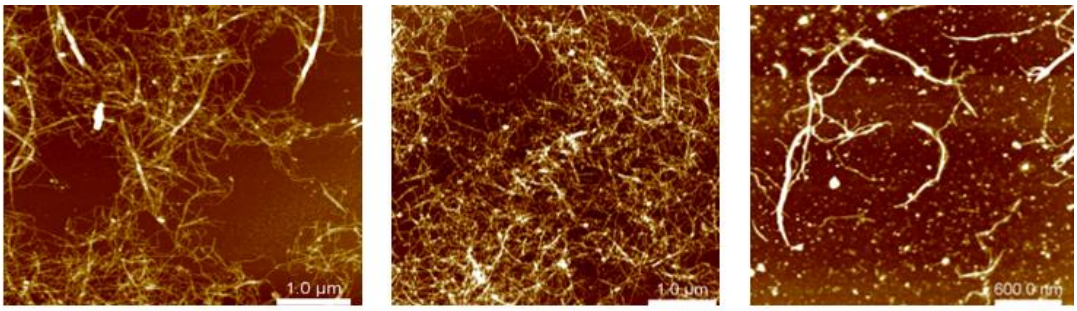
the homogenizer and obtained more gel-like slurry. (Khalil, Davoudpour et al. 2014). However, it is impossible to disintegrate cellulose into individual fibrils completely as shown in Figure 38 because numbers of hydrogen bonds are still present.



a) b) c)

Figure 38 SEM images (1000x magnification) of a) Microfluidized-Homogenized-TEMPO-oxidized recycled fiber at low oxidation (M-H-TO_low) b) Microfluidized-Homogenized TEMPO-oxidized recycled fiber at high oxidation level (M-H-TO_high) and c) Microfluidized-Homogenized-carboxymethylation of recycled fiber (M-H-Car)

The average width of nanofibirls from two modification techniques yielded the filaments with the width varied from 2-15 nm and the length in several microns as shown in Figure 39.



a) b) c)

Figure 39 AFM images of a) M-H-TO_low b) M-H-TO_high, and c) M-H-Car

4.3 Mechanical properites of filaments and characterization

The mechanical strengths of spun fibers mainly depended on the orientation of CNF and the compositions. The CNF produced from TEMPO-oxidized recycled contained

lignin and hemicellulose which directly affect the homogeneity and also weaken the fiber. The result from this thesis also correlated with the previous study from Ma et al. 2015 that the lignin and hemicellulose in fiber decrease the mechanical strength of spun filament (Ma, Hummel et al. 2016). In addition, the 100% CNF (virgin pulp) filament illustrated more homogeneous compared to the filament spun from the 100% TEMPO-oxidized recycled fiber (shown in Figure 40).

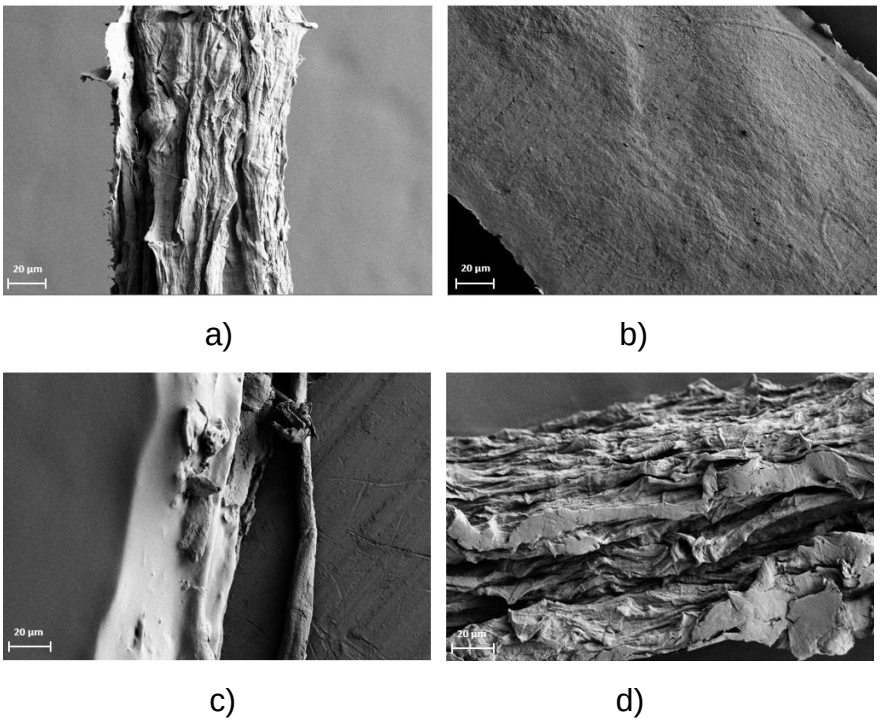


Figure 40 Spun filament from a) 100% M-H-TO_high b) 100% M-H-CNF from virgin pulp c) 10% CNF from virgin pulp + 90% CNF from 100% M-H-TO_high d) 10% PVA + 90% CNF from 100% M-H-TO_high

The dry and wet tensile strength of all spun filaments at different compositions were shown in Figure 41. The dry tensile strength of all samples were higher than wet strength, since the significant lower numbers of hydrogen bonds in the wet stage. Interestingly, all filaments made from recycled fiber exhibited lesser decrease in mechanical strength under wet condition. The lignin content in recycled fiber and hornification effect delayed water absorption to filaments resulting in less decreasing in mechanical strength (Ma, Hummel et al. 2016).

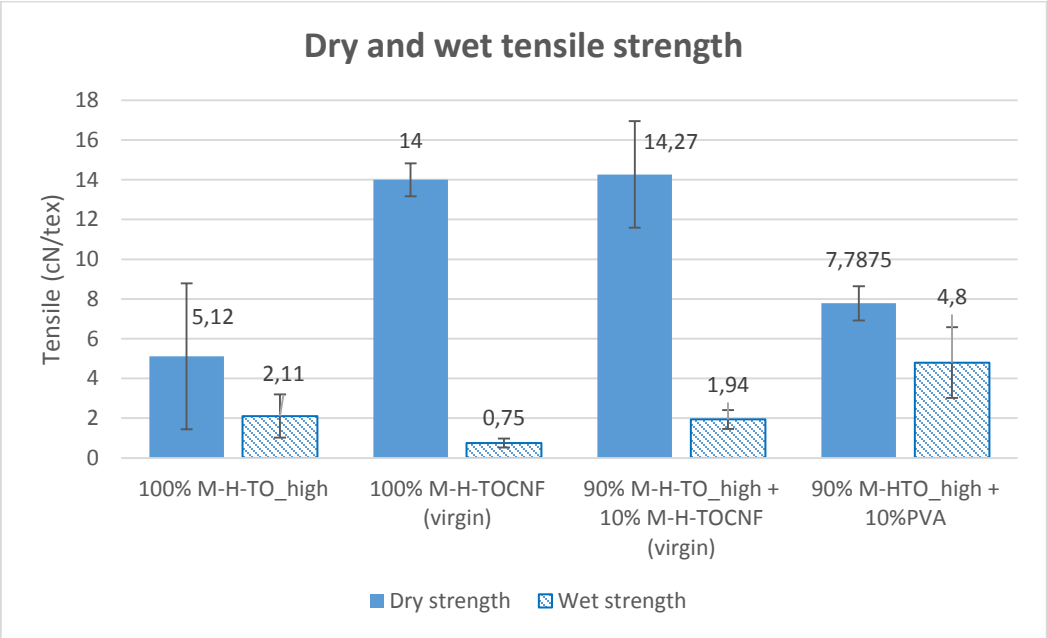


Figure 41 Dry and wet tensile strength of spun filaments

Additional of two additives (TOCNF, and Polyvinyl alcohol; PVA) to filaments enhanced the tensile strength. M-H-TO_high composite filament showed significantly higher tensile compared to the TO_high-PVA composite filament. The orientation of cellulose (from SEM) in TOCNF illustrated more homogeneous than the TO_high-PVA. However, the drawn TO_high-PVA filament also improved the tensile strength as previously reported by Endo et al. 2013 and Virtanen et al. 2014. PVA was widely used in industry as reinforcing agent and provided high strength as well as modulus. The reinforcing potential from PVA was explained by the crosslinking between the fibrils and functional groups of PVA. The spun TO_high-PVA filament also exhibited higher water retardant from moisture as the wet tensile strength slightly decreased compared to the TO_high-CNF composite filament (Virtanen, Vuoti et al. 2014, Endo, Saito et al. 2013).

The comparison of mechanical strength of spun filament with those from Ma et al 2015. The filaments produced from wet spinning technique has inferior mechanical strengths than the filaments from Lyocell method (dissolution of fiber in ionic liquid). All of the spun filaments from Lyocell yielded the tenacities (tensile strength) in the range of 30-40 $cNtex^{-1}$, as shown in Figure 42, while the tensile strength was in the range of 10-

15 $cNtex^{-1}$. However, the tensile strength of spun filament from two different techniques could not directly compared, since the ionic liquid partially liberated the strength the spun fiber by resisting the elongational stress during spinning process (Ma, Hummel et al. 2016). In addition, the overall strength of the filaments from Lyocell were still lower than those spun from the commercial dissolving pulp.

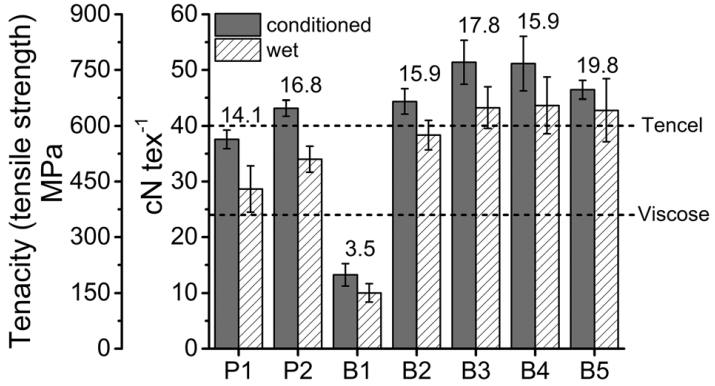


Figure 42 the mechanical strength of spun filament from fine paper: P1-P2 cardboard B1-B5 (Ma, Hummel et al. 2016)

4.4 Mechanical properties of paper

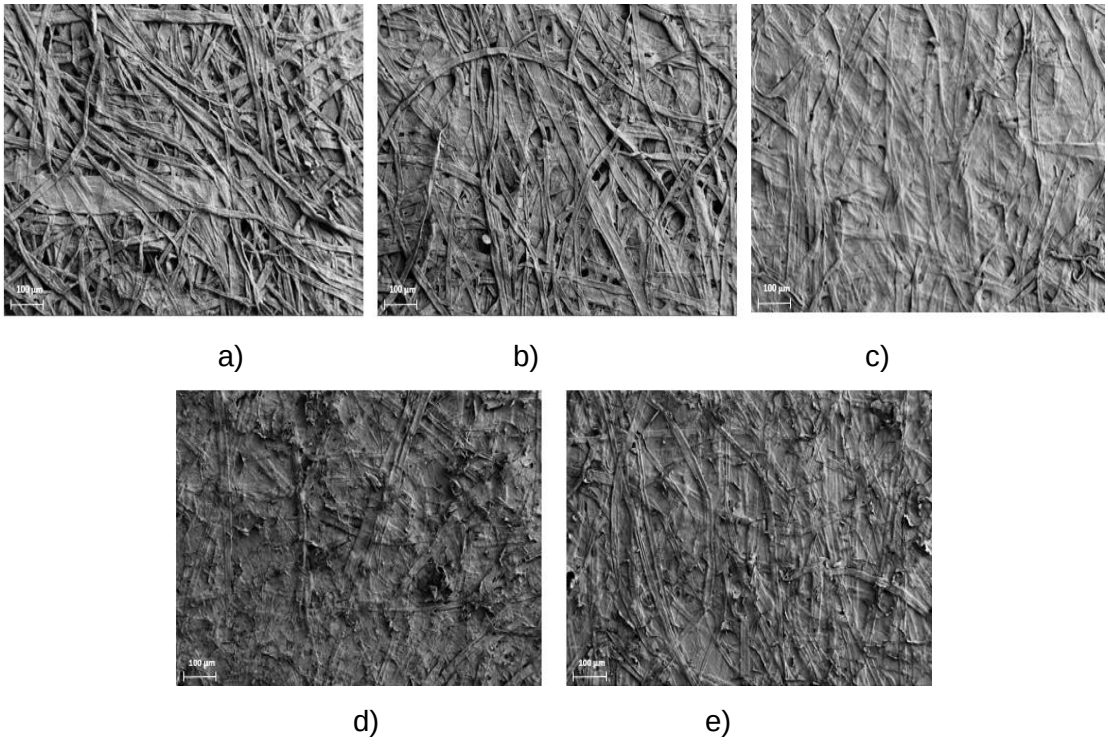
Cellulose nanofibril was utilized as strength additives in paper by direct addition into pulp slurry. The mechanical treatment for three additives were presented in Table 5.

Table 5 Different mechanical treatments used for additives in paper

	Homogenization	**Microfluidization**
H-TO_low	Yes	No
M-H-TO_high	Yes	Yes
M-H-Car	Yes	Yes
CNF (virgin)	Yes	Yes

Porosity of papers were decreased with additional of all additives, especially for microfluidized additives. The CNF, produced from TEMPO-oxidized at high oxidation, carboxymethylation, and CNF (virgin), tend to form compact structure and close the void spaces between fibers resulting in significantly decrease in pore volume. Moreover, fines and external surface fibrils also enhance the formation of dense

structure and enclose other empty spaces. Moreover, the surface roughness of paper has not been affected from CNF. The results from this thesis also correlates with the earlier study from Delgado-Aguilar et al. 2015 studying the utilization of CNF in deinked pulp suspension (Delgado-Aguilar, Tarrés et al. 2015). The SEM images confirm the morphological and structural of papers that the structure of papers with additives have dense and less porosity surface (Sehaqui, Ezekiel Mushi et al. 2012) as shown in Figure 43.



a) b) c)

d) e)

Figure 43 SEM images of papers at 100x magnification a) control b) H-TO_low c) M-H-TO_high d) M-H-Car e) CNF (virgin)

The tensile index refers to the potential resistance to web breaking of paper. The TEA index indicates the durability of paper subjected to repetitive stressing. The tensile stiffness index showed stiffness of paper. Three mechanical properties (tensile index, TEA index, and tensile stiffness index) were significantly improved after addition of homogenized and microfluidized samples. The 25% M-H-Car sample exhibited highest improvement, since the carboxymethylated fiber exhibited the better dispersibility reported earlier by Naderi et al. 2015 (Naderi, Lindström et al. 2015). The

steric hindrance effect from methyl groups in carboxymethylated fiber also prevented the aggregation of CNF during the sheet forming and the drying process. As a result, improved mechanical strengths have been observed in all samples with strength additives as shown in Figure 44. Moreover, the results from this study were consistent with those reported previously by Eyholzer et al. 2010 (Eyholzer, Bordeanu et al. 2010).

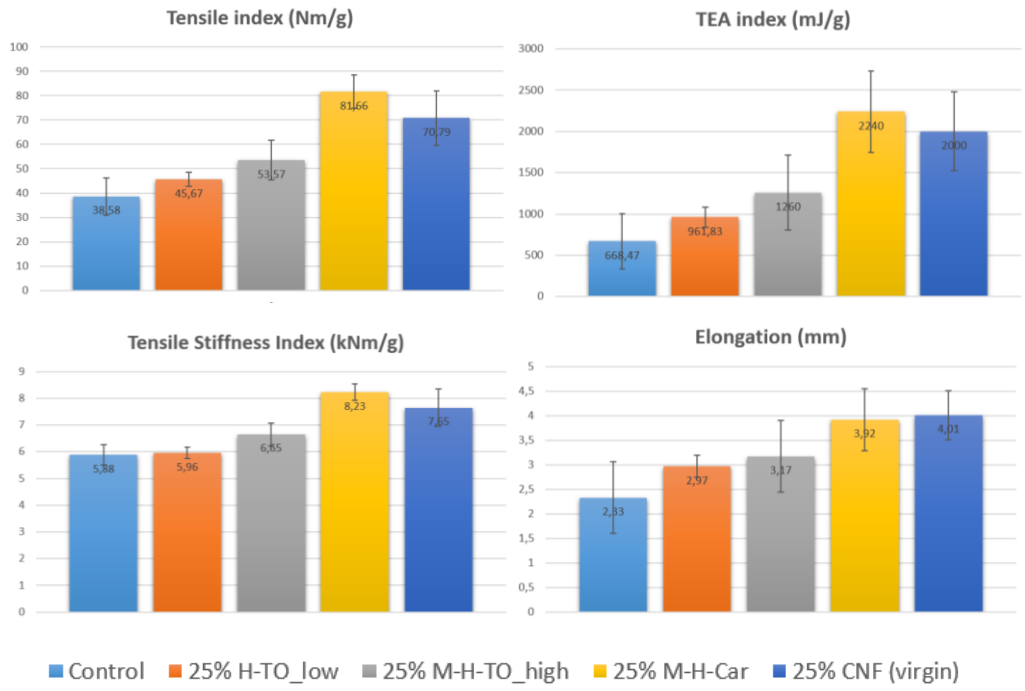


Figure 44 Tensile index, TEA index, tensile stiffness index, and elongation of all paper specimens

The strength of the paper with homogenized TEMPO-oxidized fiber illustrated lower mechanical strength compared to the paper with microfluidized recycled fiber. This can be explained from the lower specific surface area of fiber after homogenization. The microfluidized recycled fiber theoretically improves mechanical strength of paper by many factors: higher surface area of nanofibrils boost numbers of inter-fibrils adhesion in paper, excellent distribution of fibrils in paper resulting in uniform distribution of stress, and less void space inside paper structure generating lower numbers of failure-starting area. Moreover, papers with additives illustrated higher elongation due to more stiffness of paper from CNF. This result agrees well with those

observed earlier by Eyholzer at al. 2010 and Henriksson et al. 2008 (Eyholzer, Bordeanu et al. 2010, Henriksson, Berglund et al. 2008).

The result from this study also similar to those reported by Laine et al. 2000. The addition of carboxymethylated pulp, as dry strength additive, increases mechanical strength of paper. The main factors influencing paper strength relate to fiber-fiber bond strength and bonding area. In this thesis, the microfluidized carboxymethylated recycled fiber illustrated higher specific surface area while in the study of Laine et al. 2000 have utilized unfibrillated pulp, thus more bonding area can be formed in this thesis (Laine, Lindstrom et al. 2000).

The carboxymethylated recycled fiber also demonstrated high stiffness. The suitable application would be related to sack kraft and shopping bag paper. These papers need to have higher tensile strength and stiffness to their applications. Therefore, the paper needs to be strong enough to resist tough handling. It must be assumed that the sacks will be handled roughly, for instance, when unloaded from a lorry and thrown to the ground. (Paulapuro 2000).

Chapter 5 Conclusions

In this study, recycled fiber obtained from waste cardboard was pretreated with TEMPO- oxidation or Carboxymethylation methods. The recycled fibers were introduced various amount of carboxylic groups on the surface of fibers. Three characterization techniques confirms the presence of carboxylic groups by Scanning Electron Microscope (SEM), Conductometric titration, and Fourier Transform Infrared Spectroscopy (FTIR). Then, the pretreated recycled fibers were isolated into nanofibrils by homogenizer and microfluidizer. The carboxymethylated recycled fiber with the acidic content of 0.19 mmol/g requires higher mechanical energy, since there are lower repulsive force at the surface of fiber. The Atomic Force Microscopy and SEM were used to identify the morphology of CNF. The isolated nanofibrils from three treatments (TEMPO-oxidation at low oxidation level, TEMPO-oxidation at high oxidation level, and carboxymethylated recycled fiber) have the width from 2-15 nm and length in several microns.

The ensuing CNF was employed in two applications, filament forming and strength additives in paper. The continuous filaments were successfully spun from 100% recycled fiber obtained from TEMPO-oxidation. Since the spun filament from 100% recycled fiber yielded low mechanical properties, two additives (CNF from virgin pulp and PVA) were added in order to enhance the mechanical strength of filaments. The spun filament from 100% TEMPO-oxidation (high) had inferior dry tensile strength compared to 100%CNF from virgin pulp due to lignin and hemicellulose presented in recycled CNF. However, the filaments from 100%TEMPO-oxidation (high) showed better wet tensile strength, since the lower sensitivity to moisture compared to 100% CNF from virgin pulp. The addition PVA as additive not only increased the dry tensile strength of spun filament but also reduced the sensitivity of filament to water.

The nanofibrils, produced from TEMPO-oxidation and carboxymethylation, as strength additive in papermaking also significantly enhanced the overall strength of paper with 25% addition based on dried content. The tensile index, TEA index, and tensile stiffness index of nanofibrils, produced from carboxymethylated recycled fiber, increased up to 111%, 235%, and 40%, respectively, compared to the control. However, long drainage of during sheet-forming posed the challenge of utilizing CNF

as a strength additive. Optimization of dosage could solve the drainage problem. The potential application of nanofibrils in packaging paper would be related to high strength papers i.e. sack kraft paper, corrugated packaging, and multi-walls sack.

5.1 Further research

5.1.1 Pretreatment

TEMPO-oxidation is the conventional pretreatment and can be operated in laboratory to obtain CNF. The high production costs make TEMPO oxidation unfavorable for the paper industry. However, other techniques (micro-emulsion, or deep eutectic solvent) offer interesting alternatives to pretreat cellulosic fiber.

5.1.2 Spun filament

According to the time constraint in this thesis, several parameters remain to be studied related to the quality of the spun filaments. The %solid of CNF, spinning rate, and solvent in coagulation bath need to be studied in order to optimize mechanical strength. Moreover, contaminant removal of recycled fiber may enhance the overall mechanical strength of spun filament as well.

As an advantage for this process, there is no effluent produced and the solvent in coagulation bath can be reused.

5.1.3 Strength additive in paper

The only challenge is the slow drainage during the sheet-forming process. Optimization of the dosage of CNF may enhance the drainage of paper, adding some wet-end chemicals (i.e. aluminium sulfate to promote drainage). Process parameters could be adjusted for good runnability.

Reference

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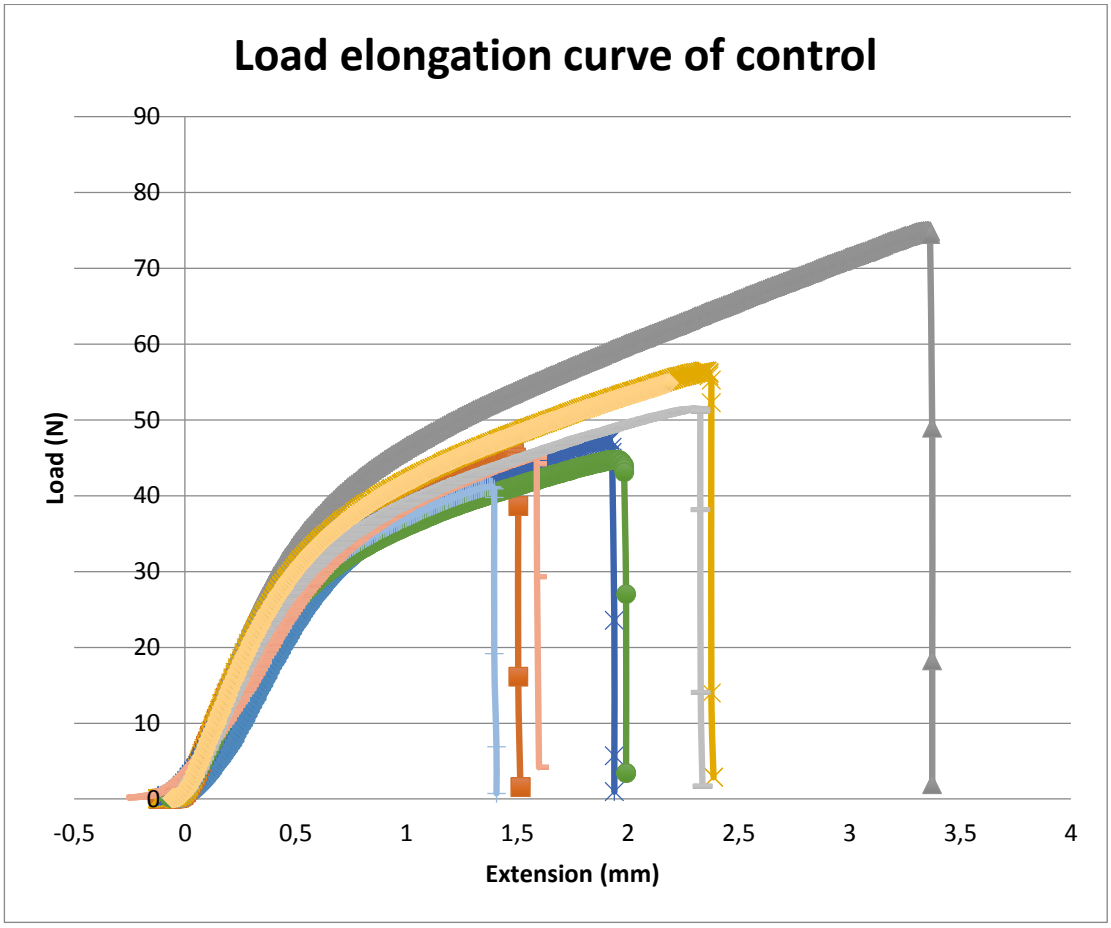
Table1 Evaluation of basic morphological and mechanical properties

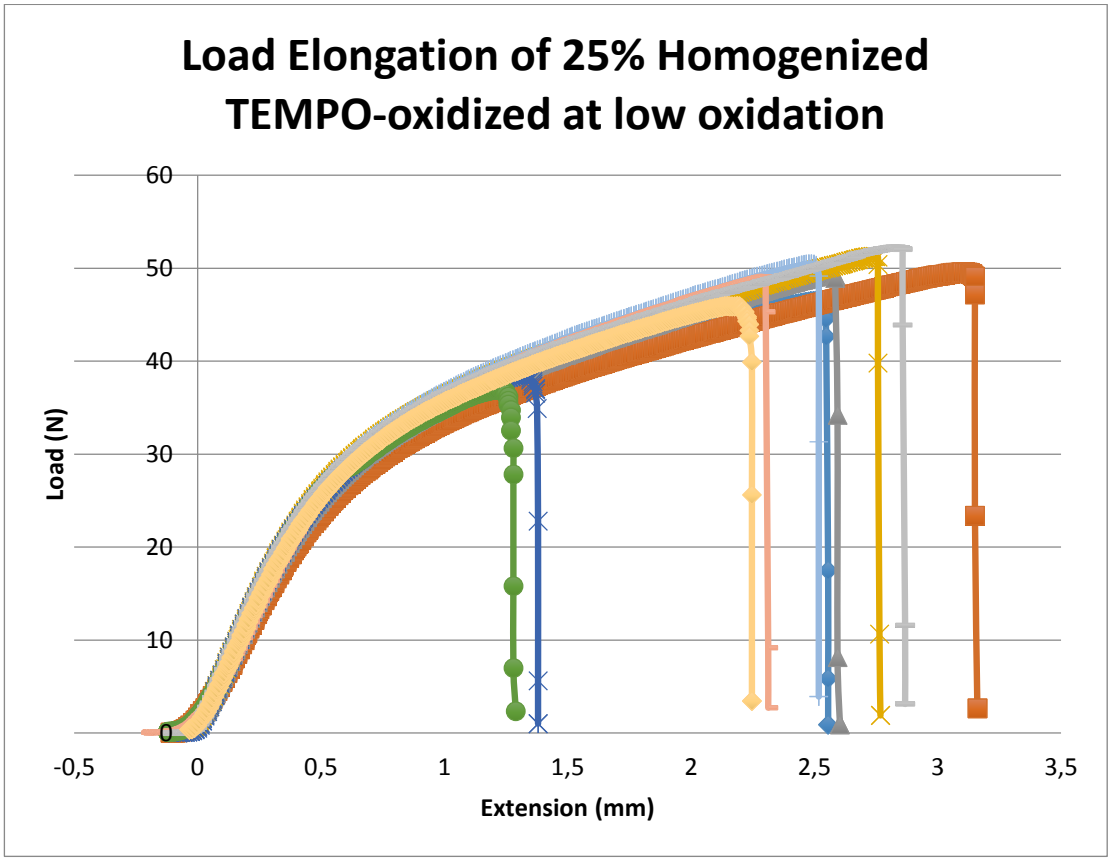
	Grammage (g/m2)		Thickness (micron)		Porosity (ml/min)		E-Modulus		Roughness (ml/min)	
	AVG	SD	AVG	SD	AVG	SD	AVG	SD	AVG	SD
Control	83.9	-	130.75	-	538	29.80	3.90	0.25	1040	78.2
25% H-TO_low	78.3	-	125.00	-	325	39.30	3.74	0.14	1131	75.9
25% M-H-TO_high	70.6	-	96.50	-	10,6	2.50	4.79	0.30	1106	50.9
25% M-H-Car	89.4	-	117.50	-	10,4	2.80	6.28	0.24	1081	230.1
25% CNF (virgin)	92.8	-	123.25	-	10,9	3.00	5.76	0.52	1367	186.6

	Tensile index (Nm/g)		Elongation (mm)		TEA index (mJ/g)		Tensile Stiffness Index (kNm/g)	
	AVG	SD	AVG	SD	AVG	SD	AVG	SD
Control	38.58	7.53	2.33	0.73	668	334	5.88	0.38
25% H-TO_low	45.67	2.84	2.97	0.22	961	121	5.96	0.22
25% M-H-TO_high	53.57	8.16	3.17	0.73	1260	453	6.65	0.42
25% M-H-Car	81.66	6.86	3.92	0.63	2240	490	8.23	0.31
25% CNF (virgin)	70.79	11.10	4.01	0.50	2000	477	7.65	0.69

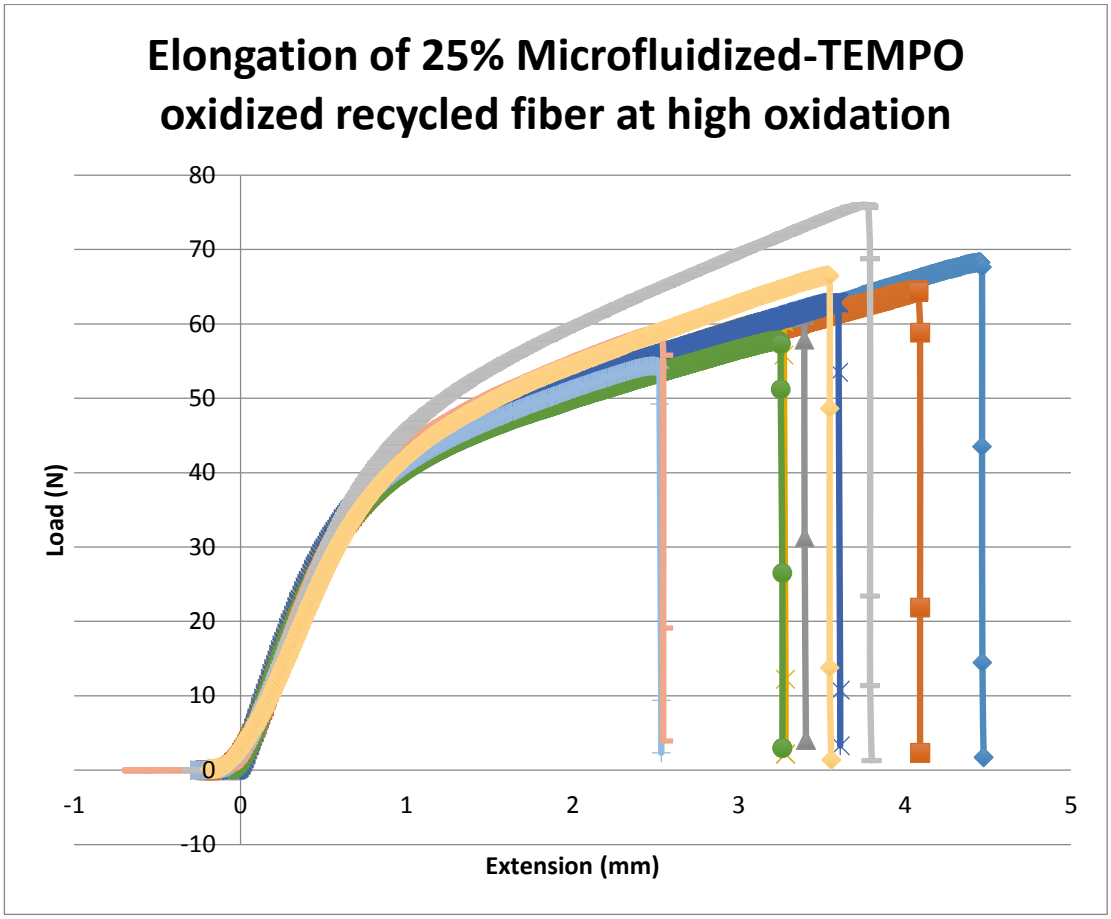
Appendix 2: Load elongation of control paper



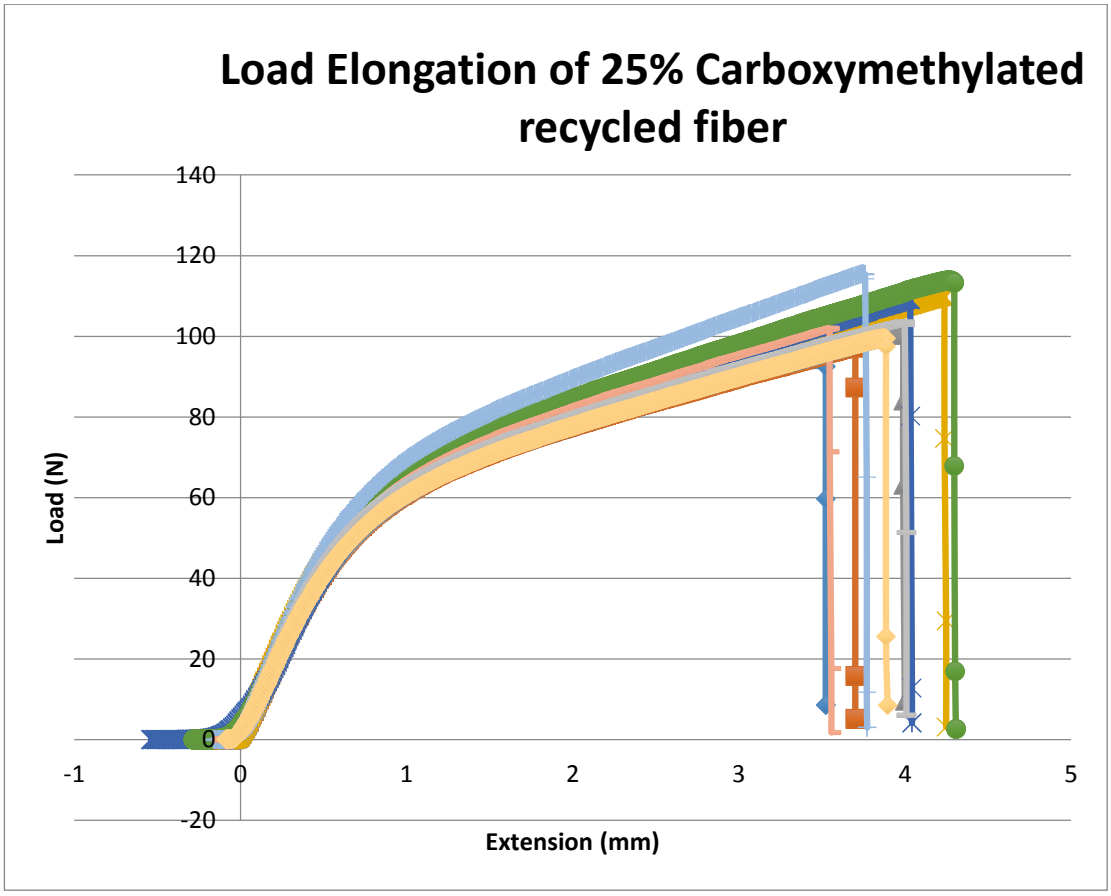
Appendix 3: Load elongation of 25% Homogenized TEMPO-oxidized recycled fiber at low oxidation



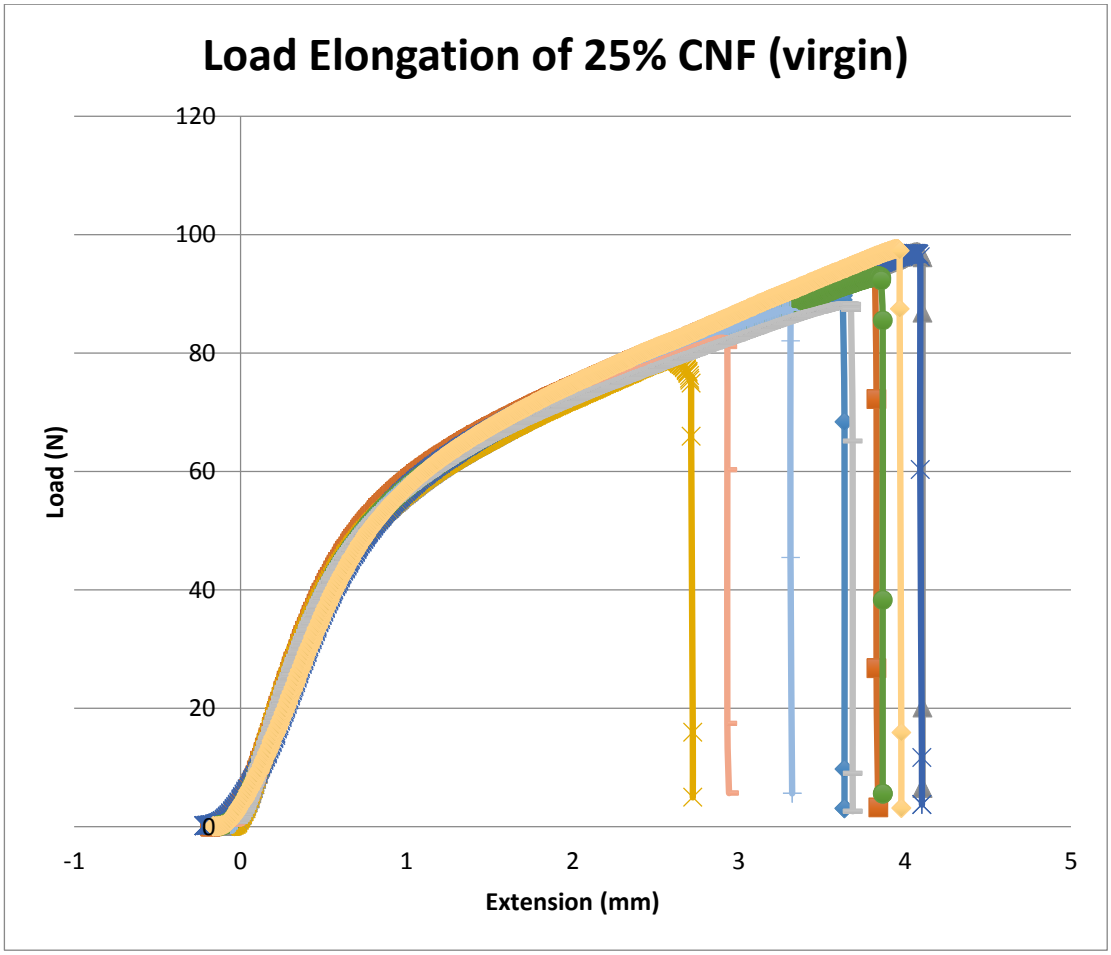
Appendix 4: Load elongation of 25% Microfluidized TEMPO-oxidized recycled fiber at high oxidation



Appendix 5: Load elongation of 25% Carboxymethylated recycled fiber



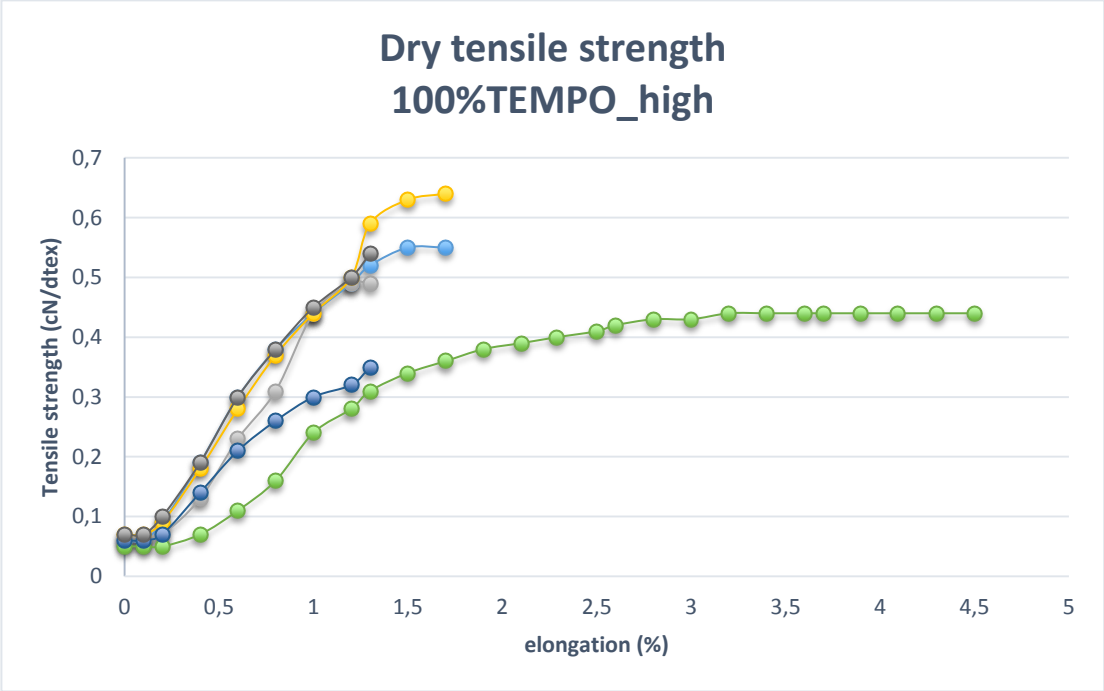
Appendix 6: Load elongation of 25% Cellulose naofibrils from wood

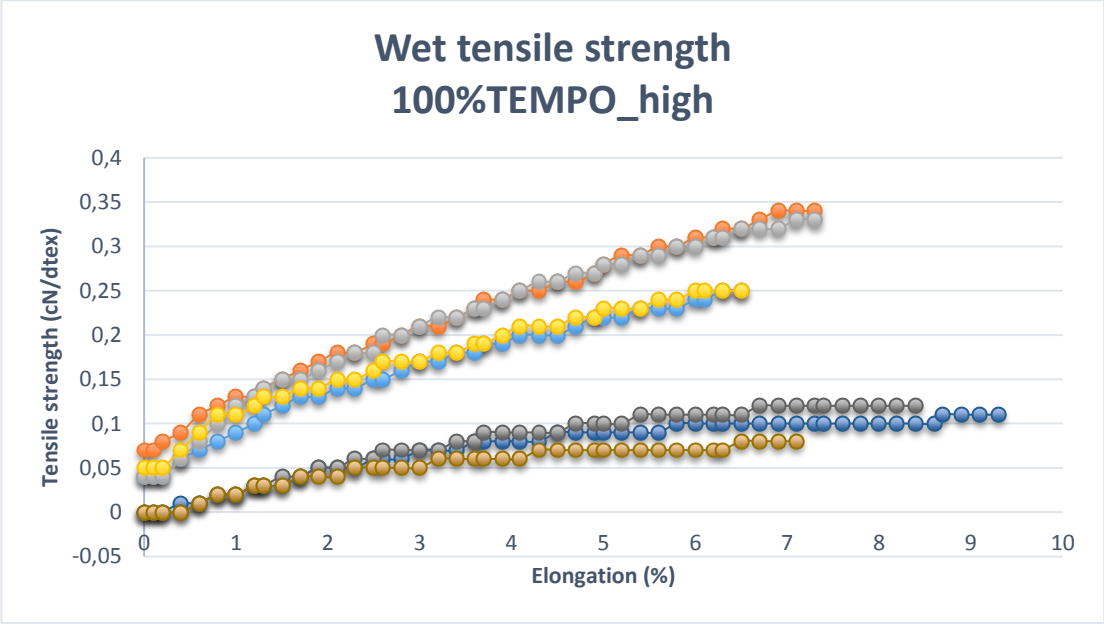


Appendix 7: Mechanical strength of continuous filaments

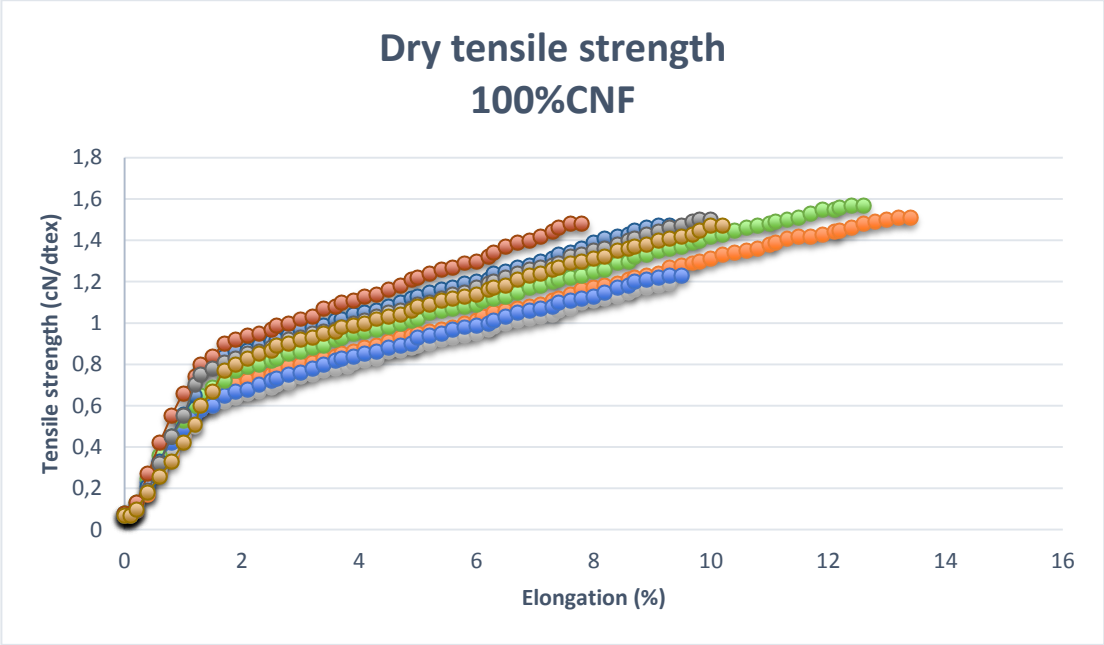
	Dry tensile strength							
	Titer		Force		Elongation		Tensile	
	dtex	SD	cN	SD	%	SD	cN/tex	sd
100%TEMPO_high	110,91	0	48,32	16,2	2,79	17,76	4,36	3,67
100%CNF (virgin)	85,21	0	113,74	4,79	9,26	25,14	13,27	2,71
10%CNF (virgin)	112,5	0	58,88	23,44	3,63	36,96	5,41	2,68
10%PVA	141,14	0	98,09	3,89	5,11	20,88	6,93	2,59
	Wet tensile strength							
	Titer		Force		Elongation		Tensile	
	dtex	SD	cN	SD	%	SD	cN/tex	sd
100%TEMPO_high	96,56	0	18,14	17,56	6,15	11,7	1,81	2,42
100%CNF (virgin)	87,92	0	6,93	8,86	4,1	1,34	0,8	2,27
10%CNF (virgin)	106,65	0	15,62	20,5	6,61	9,63	1,43	2,94
10%PVA	147,29	0	70,58	10,08	11,85	5,14	4,8	1,78

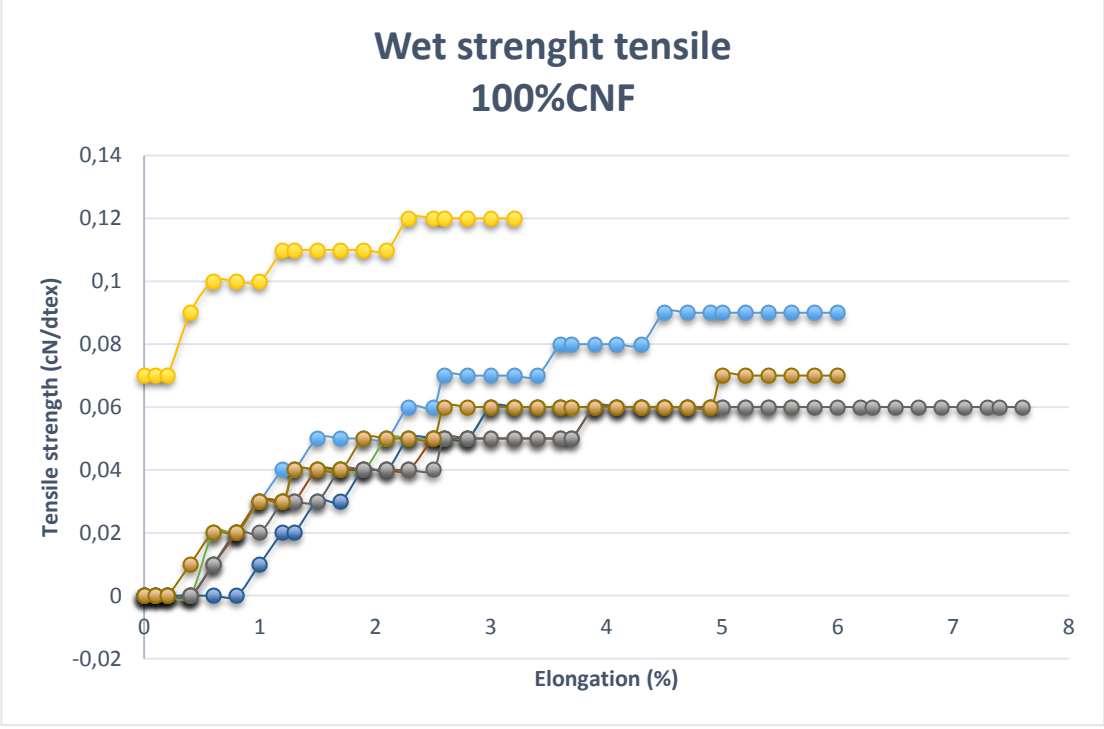
Appendix 8: Dry and Wet tensile strength of the 100%TEMPO_high filament



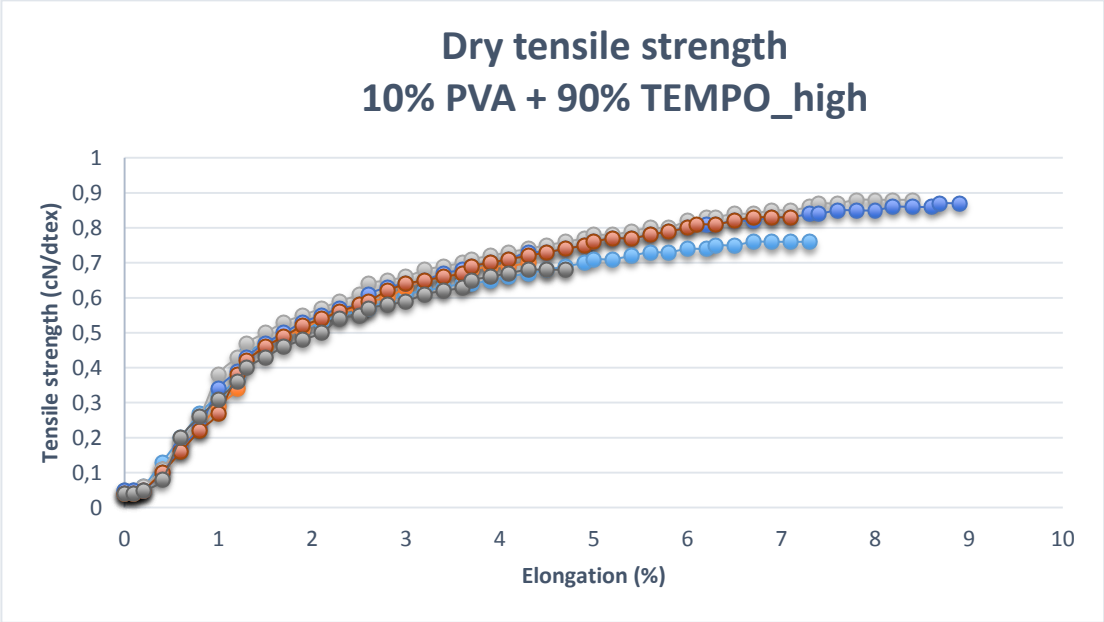


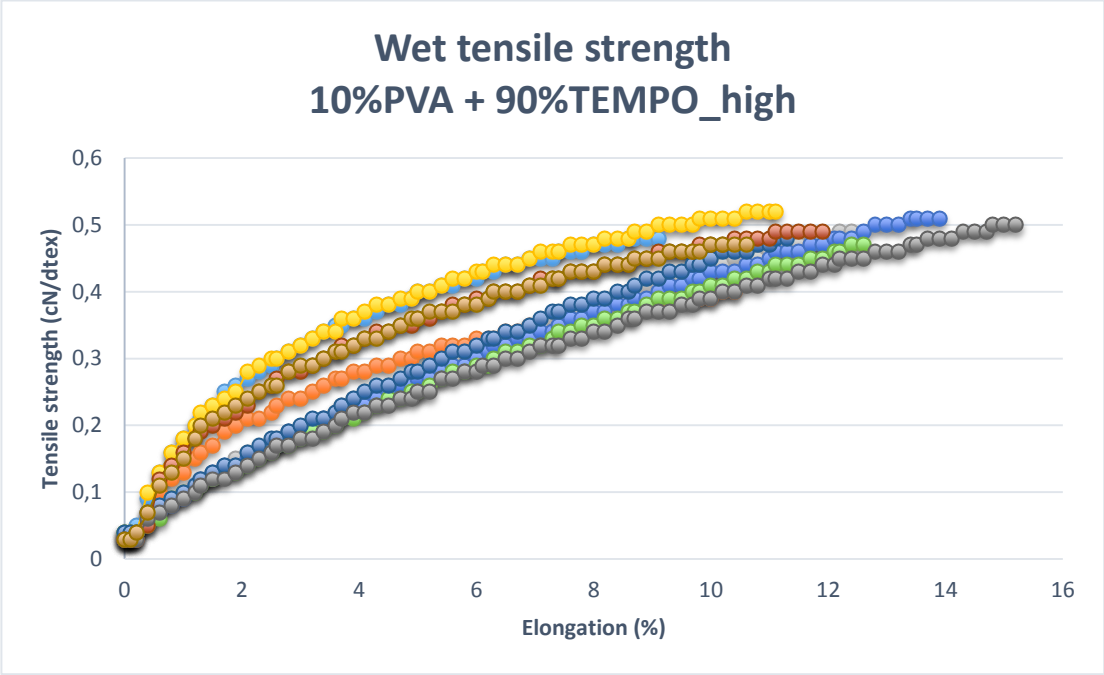
Appendix 9: Dry and Wet tensile strength of the 100%CNF filament



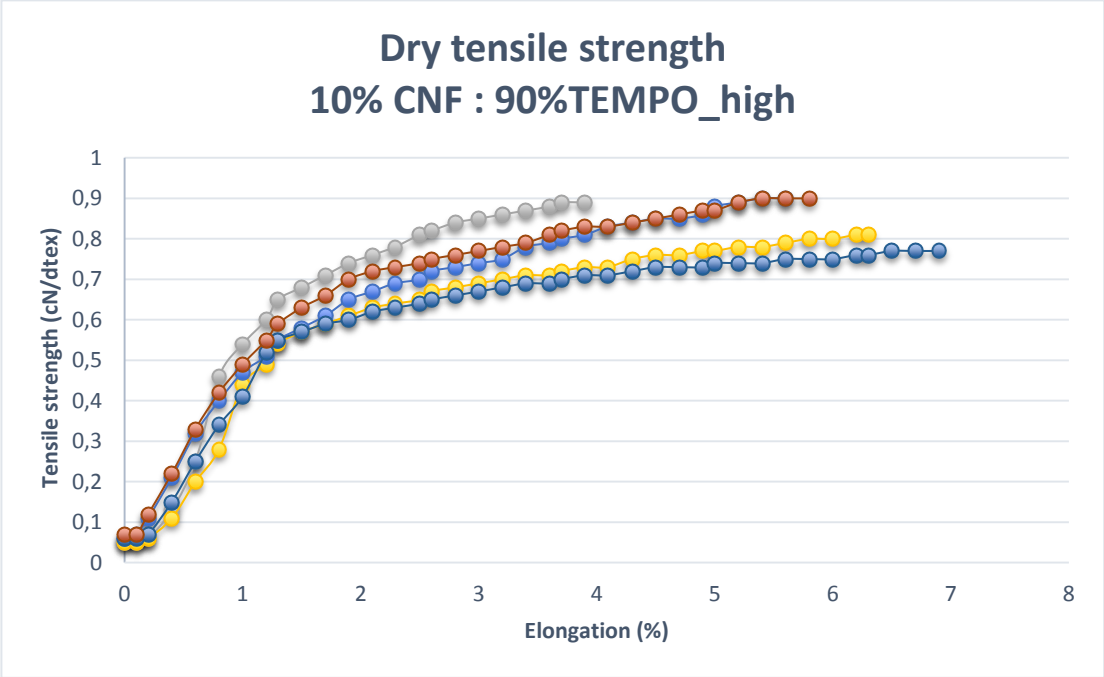


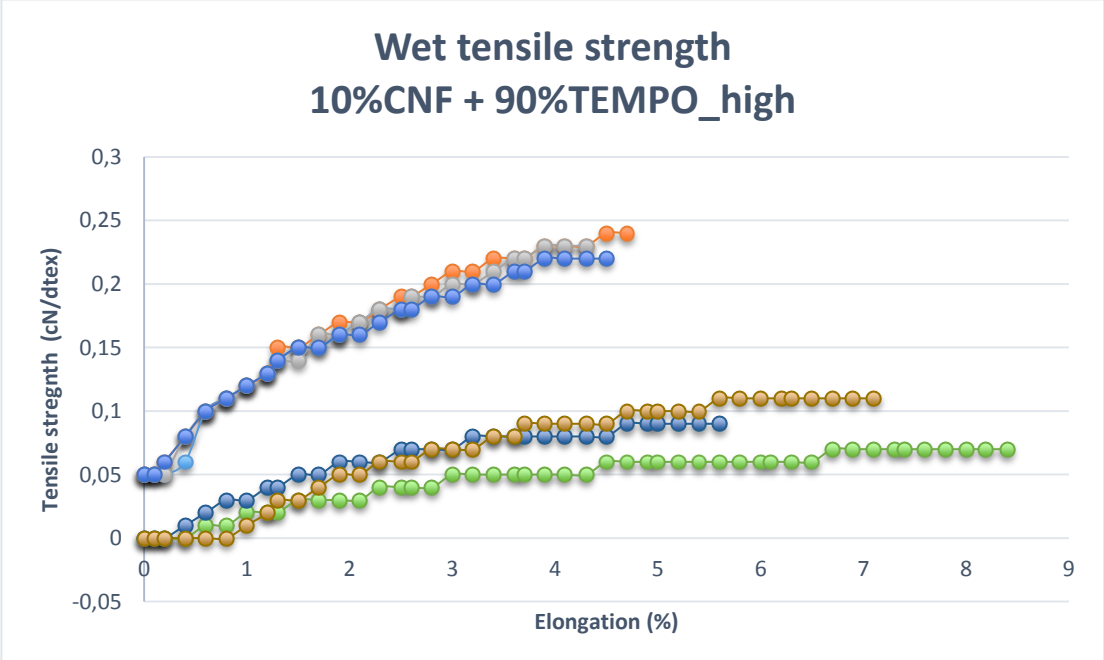
Appendix 10: Dry and Wet tensile strength of the 10%PVA + 90%TEMPO_high





Appendix 11: Dry and Wet tensile strength of the 10%CNF + 90%TEMPO_high





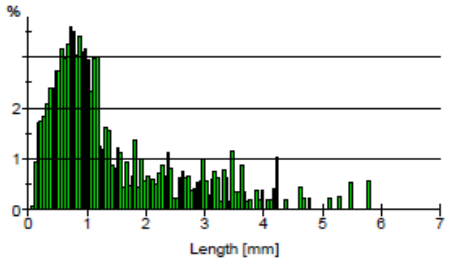
Appendix 11: Fiber length and distribution of recycled fiber

FiberLab™

Summary Report, Length

Sample name	Sample date
Recycled fiber	03-05-16 10:45
Analysed by	**Sample ID**
Metso Automation	000 - <none>
Analysed date	**Notes**
02/06/16 21:26	Standard:[TAPPI]

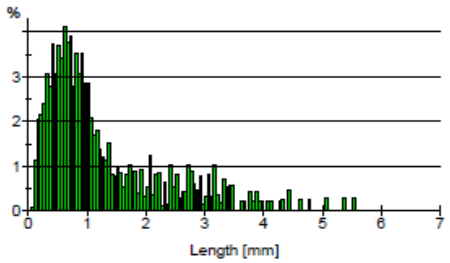
Fiber length - weighted distribution



Length results:	Cont	Proj	
L(n)	0.66	0.58	mm
L(l)	1.43	1.26	mm
L(w)	2.40	2.18	mm
Fines(n)	25.99	27.32	%
Fines(l)	4.48	5.38	%
Fibers measured		3151	pcs
Length range		0.00 - 7.60	mm

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	5780	pcs

Proj. length - weighted distribution



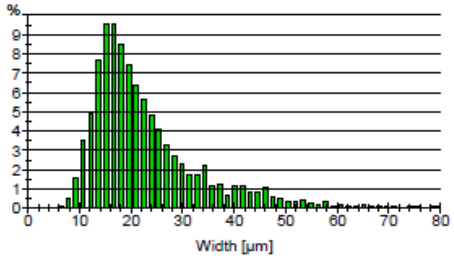
Wood species: <none>

	Cont	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

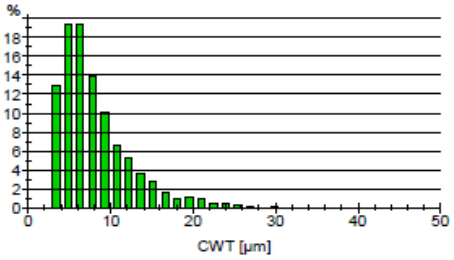
Width distribution



Length weighted fractions:

mm	Fr (l)	Fr p(l)	
0.00 - 0.20	4.48	5.38	%
0.20 - 0.50	14.11	18.72	%
0.50 - 1.20	41.55	40.73	%
1.20 - 2.00	14.94	13.53	%
2.00 - 3.20	14.34	14.44	%
3.20 - 7.60	10.59	7.20	%

Fiber CWT distribution



Fiber width:	20.1	µm
Fiber CWT:	5.5	µm
Fibers Imaged:	2340	pcs
Width range:	1.5 - 147.0	µm
CWT range:	1.5 - 147.0	µm
Vessels:	88.54	1/m
Vessels:	58.08	1/1000 fibers
Vessels total:	183	pcs

metso

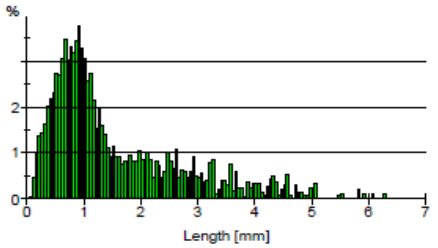
Appendix 8: Fiber length and distribution of TEMPO-oxidized recycled fiber at low oxidation level

FiberLab™

Summary Report, Length

Sample name	Sample date
TEMPO_low	03-05-16 10:45
Analysed by	**Sample ID**
Metso Automation	000 - <none>
Analysed date	**Notes**
02/06/16 20:46	Standard:[TAPPI]

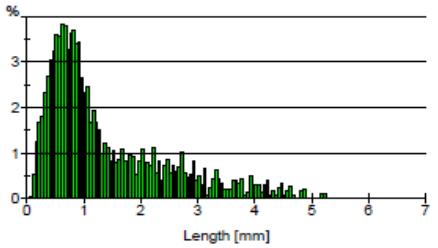
Fiber length - weighted distribution



Length results:	Cont	Proj	
L(n)	0.76	0.67	mm
L(l)	1.51	1.34	mm
L(w)	2.45	2.20	mm
Fines(n)	17.46	18.84	%
Fines(l)	2.83	3.49	%
Fibers measured		7875	pcs
Length range		0.00 - 7.60	mm

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	19607	pcs

Proj. length - weighted distribution



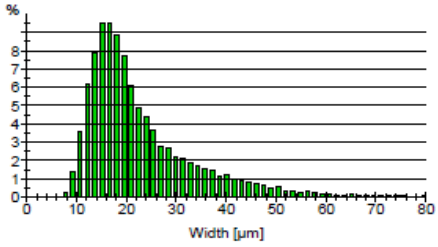
Wood species: <none>

	Cont	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

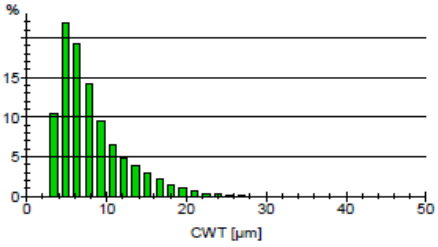
Width distribution



Length weighted fractions:

mm	Fr (l)	Fr p(l)	
0.00 - 0.20	2.83	3.49	%
0.20 - 0.50	12.26	16.69	%
0.50 - 1.20	41.23	41.26	%
1.20 - 2.00	16.64	15.32	%
2.00 - 3.20	15.87	14.79	%
3.20 - 7.60	11.16	8.45	%

Fiber CWT distribution



Fiber width:	20.1	µm
Fiber CWT:	5.5	µm
Fibers Imaged:	6547	pcs
Width range:	1.5 - 147.0	µm
CWT range:	1.5 - 147.0	µm
Vessels:	81.79	1/m
Vessels:	62.48	1/1000 fibers
Vessels total:	492	pcs

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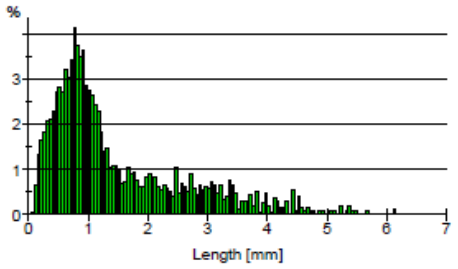
Appendix 9: Fiber length and distribution of TEMPO-oxidized recycled fiber at high oxidation level

FiberLab™

Summary Report, Length

Sample name	Sample date
TEMPO_h	03-05-16 10:45
Analysed by	**Sample ID**
Metso Automation	000 - <none>
Analysed date	**Notes**
02/06/16 14:41	Standard:[TAPPI]

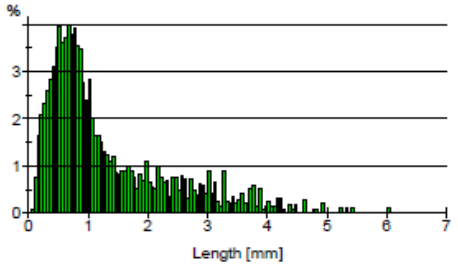
Fiber length - weighted distribution



Length results:	Cont	Proj	
L(n)	0.69	0.62	mm
L(l)	1.43	1.28	mm
L(w)	2.35	2.16	mm
Fines(n)	21.50	23.08	%
Fines(l)	3.70	4.52	%
Fibers measured		8274	pcs
Length range		0.00 - 7.60	mm

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	21476	pcs

Proj. length - weighted distribution



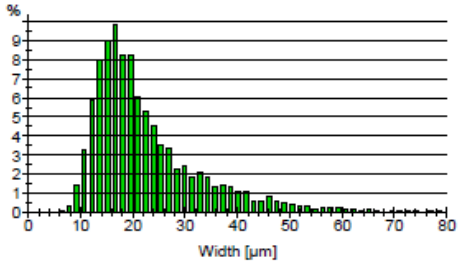
Wood species: <none>

	Cont	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

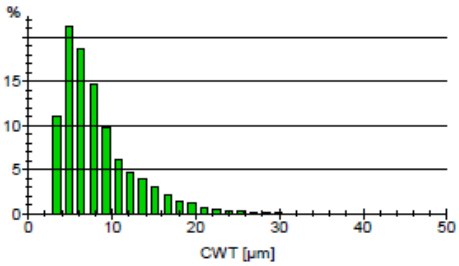
Width distribution



Length weighted fractions:

mm	Fr (l)	Fr p(l)	
0.00 - 0.20	3.70	4.52	%
0.20 - 0.50	13.88	18.33	%
0.50 - 1.20	42.23	40.82	%
1.20 - 2.00	15.15	14.77	%
2.00 - 3.20	15.09	13.86	%
3.20 - 7.60	9.95	7.70	%

Fiber CWT distribution



Fiber width:	20.1	µm
Fiber CWT:	5.6	µm
Fibers Imaged:	6488	pcs
Width range:	1.5 - 147.0	µm
CWT range:	1.5 - 147.0	µm
Vessels:	87.63	1/m
Vessels:	60.79	1/1000 fibers
Vessels total:	503	pcs

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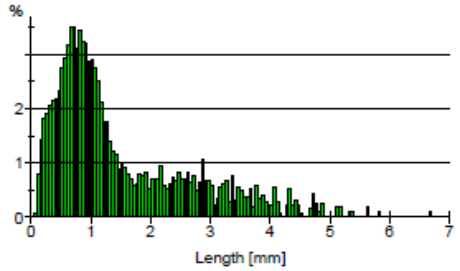
Appendix 10: Fiber length and distribution of Carboxymethylated recycled fiber

FiberLab™

Summary Report, Length

Sample name	Sample date
CMC	03-05-16 10:45
Analysed by	**Sample ID**
Metso Automation	000 - <none>
Analysed date	**Notes**
02/06/16 21:06	Standard:[TAPPI]

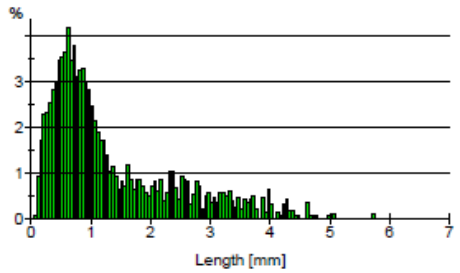
Fiber length - weighted distribution



Length results:	Cont	Proj	
L(n)	0.68	0.61	mm
L(l)	1.47	1.31	mm
L(w)	2.43	2.20	mm
Fines(n)	24.02	25.72	%
Fines(l)	4.10	4.99	%
Fibers measured		8222	pcs
Length range		0.00 - 7.60	mm

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	22559	pcs

Proj. length - weighted distribution



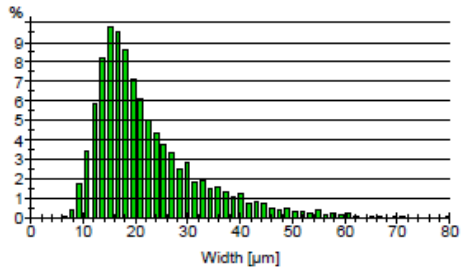
Wood species: <none>

	Cont	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

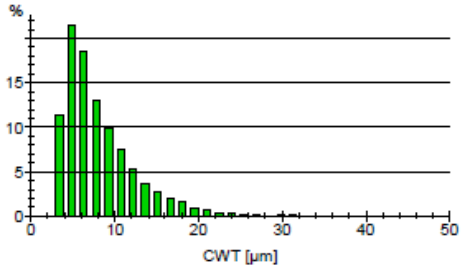
Width distribution



Length weighted fractions:

mm	Fr (l)	Fr p(l)	
0.00 - 0.20	4.10	4.99	%
0.20 - 0.50	13.34	17.62	%
0.50 - 1.20	40.99	40.24	%
1.20 - 2.00	14.63	13.58	%
2.00 - 3.20	15.65	15.11	%
3.20 - 7.60	11.29	8.46	%

Fiber CWT distribution



Fiber width:	19.7	µm
Fiber CWT:	5.5	µm
Fibers Imaged:	6243	pcs
Width range:	1.5 - 147.0	µm
CWT range:	1.5 - 147.0	µm
Vessels:	76.99	1/m
Vessels:	52.66	1/1000 fibers
Vessels total:	433	pcs

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